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16th April, 2024

Alkenes

Alkanes are non reactive, and they are called paraffins, Par = affisinus

Alkenes / Olefins → Addition reactions
① hydrogenation
② halogenation
③ hydration
④ hydrohalogenation
→ Oxidation reactions
⑤ hydroxylation
⑥ Ozonolysis
→ Polymerization

Combustion

① $C_xH_y + zO_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$

LHS = RHS

$2\alpha = 2x + \frac{y}{2}$

$\alpha = x + \frac{y}{4}$

$\therefore C_xH_y + \left(x+\frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$

② $C_nH_{2n+2} + \alpha O_2 \rightarrow nCO_2 + \frac{2n+2}{2}H_2O$

$2\alpha = 2n + \frac{2n+2}{2}$

$2\alpha = 2n + n + 1$

$2\alpha = 3n + 1$

$\alpha = \frac{3n+1}{2}$

$\therefore C_nH_{2n+2} + \frac{3n+1}{2}O_2 \rightarrow nCO_2 + \frac{2n+2}{2}H_2O$

Classwork

③ $C_nH_{2n} + eO_2 \rightarrow fCO_2 + gH_2O$

$C_nH_{2n} + \alpha O_2 \rightarrow nCO_2 + \frac{2n}{2}H_2O$

$2\alpha = 2n + \frac{2n}{2}$

$2\alpha = 2n + n$

$\alpha = \frac{3n}{2}$

Class

$\therefore \frac{3n}{2}$, $f = n$, $g = n$

Assignment

(i) $C_nH_{2n+1}OH + eO_2 \rightarrow fCO_2 + gH_2O$

(v) $C_nH_{2n+1}CHO + eO_2 \rightarrow fCO_2 + gH_2O$

find e, f and g

(vi) $C_nH_{2n+1}COOH + eO_2 \rightarrow fCO_2 + gH_2O$

Addition Reactions — Pi bonds break in addition reaction

$-C=C- \xrightarrow{A-A} -\overset{A}{\underset{|}{C}}-\overset{A}{\underset{|}{C}}-$

H–H (H_2) → Hydrogenation
X–X (X_2) – Halogenation
H–X – Hydrohalogenation
A–OH – Hydration

① $CH_3-CH=CH-CH_3 \xrightarrow{H_2/Pt} CH_3-CH_2-CH_2-CH_3$

(Anytime that's addition reaction, you use transition metal catalyst)

$CH_3-CH=CH-CH_3 \xrightarrow{Br_2} CH_3-\overset{Br}{\underset{H}{C}}-\overset{Br}{\underset{H}{C}}-CH_3$

$\xrightarrow{Cl_2} CH_3-\overset{Cl}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-CH_3$

$\xrightarrow{HBr} CH_3-\overset{H}{\underset{|}{C}}-\overset{Br}{\underset{|}{C}}H-CH_3$

$\xrightarrow{H^+/H_2O} CH_3-CH_2-\overset{OH}{\underset{|}{C}}H-CH_3$

(It must be under acidic condition)

② $CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-CH_2-CH_2-Br$ or $CH_3-\overset{Br}{\underset{|}{C}}H-CH_3$

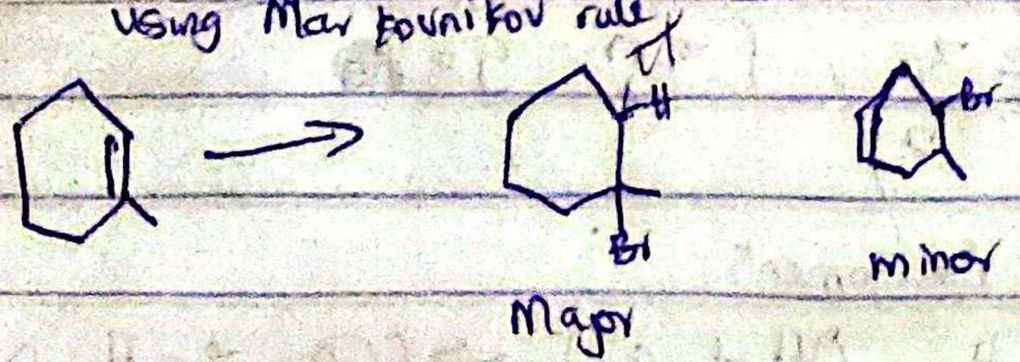
Olefic Carbon — Olefic carbon

③ $CH_3-CH=\overset{CH_3}{\underset{|}{C}}-CH_3 \xrightarrow{H^+/H_2O} CH_3-CH_2-\overset{CH_3}{\underset{OH}{\overset{|}{C}}}-CH_3$

Class

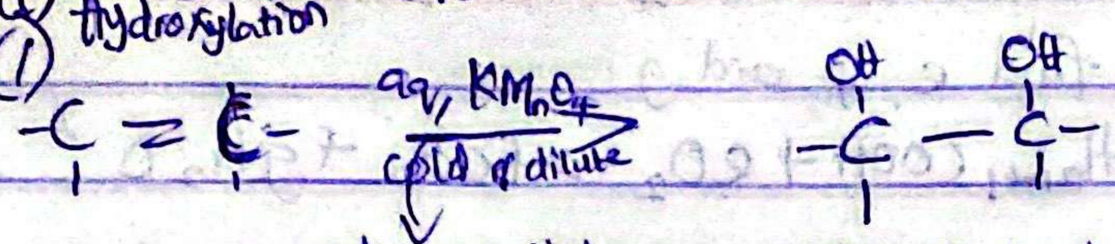
18th April, 2024

using Markovnikov rule



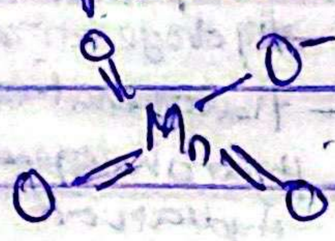
(1) Oxidation reaction

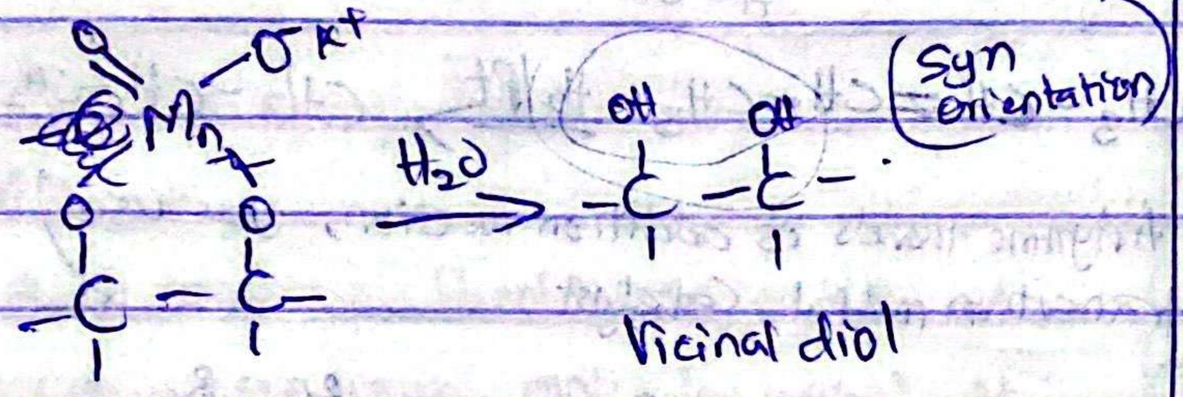
(i) Hydroxylation



whenever you see $KMnO_4$, it is called hydroxylation

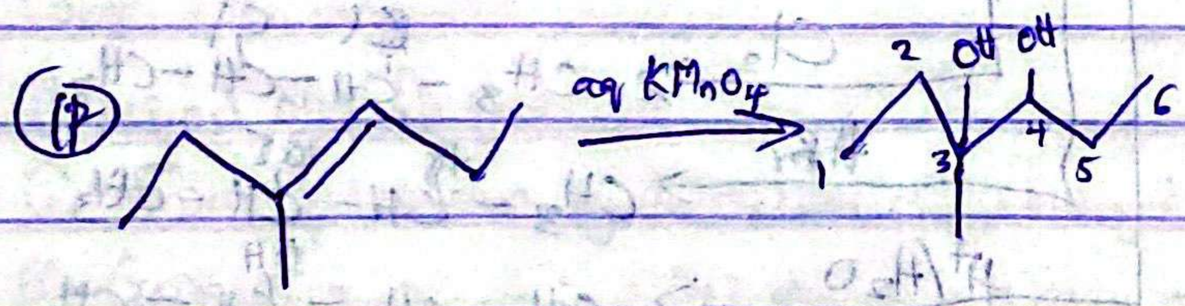
Process:





$KMnO_4$ turns brown (decolourise)

(ii)



Oxidative Cleavage

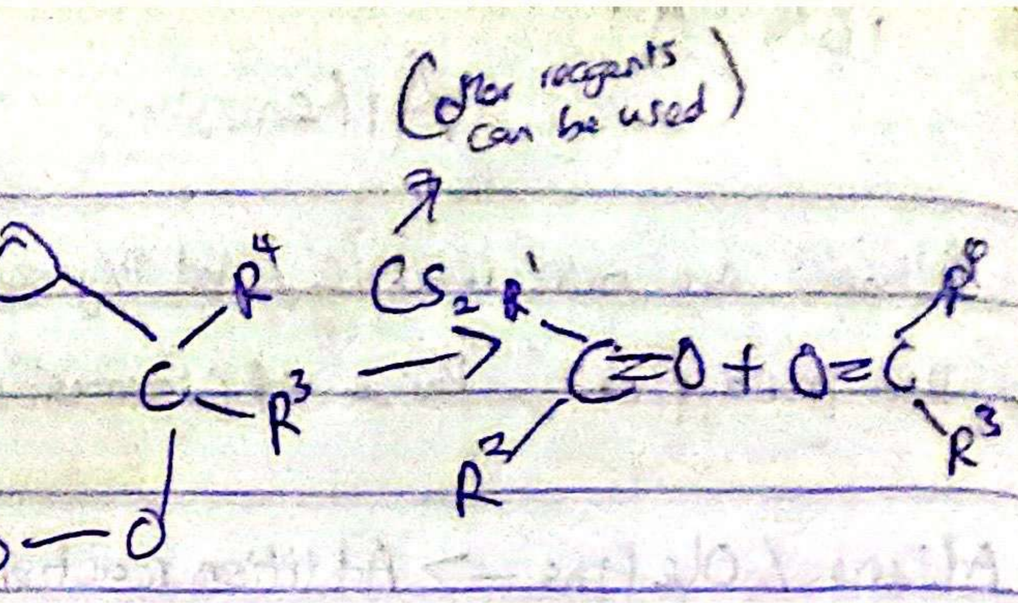
(2) Ozonolysis

This will give intermediate

(i) $R^1-C(R^2)=C(R^3)-R^4 \xrightarrow[(2)\ CS_2]{(1)\ O_3} R^1-C(R^2)=O + O=C(R^3)-R^4$

Process:

(Ozone inserts itself into the two olefinic carbon)



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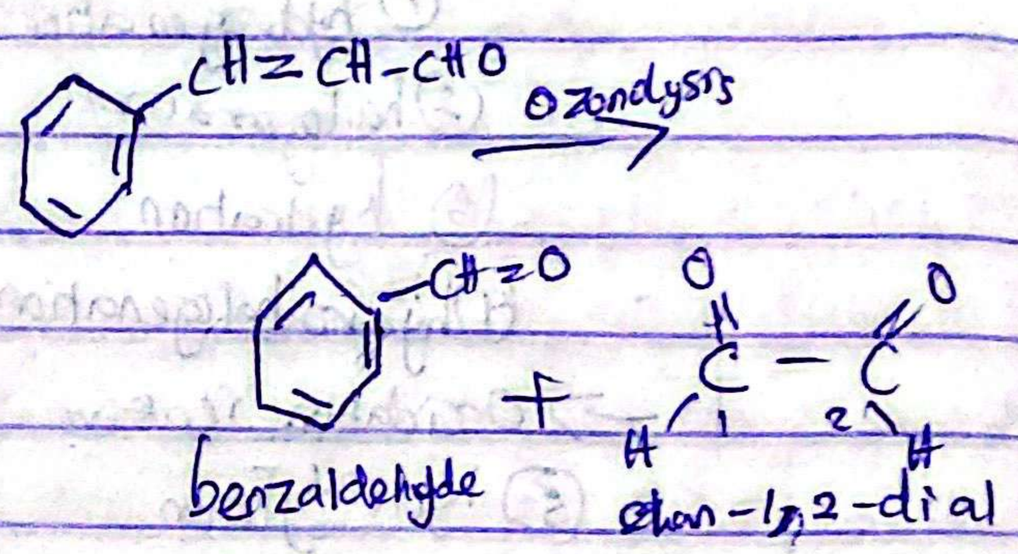

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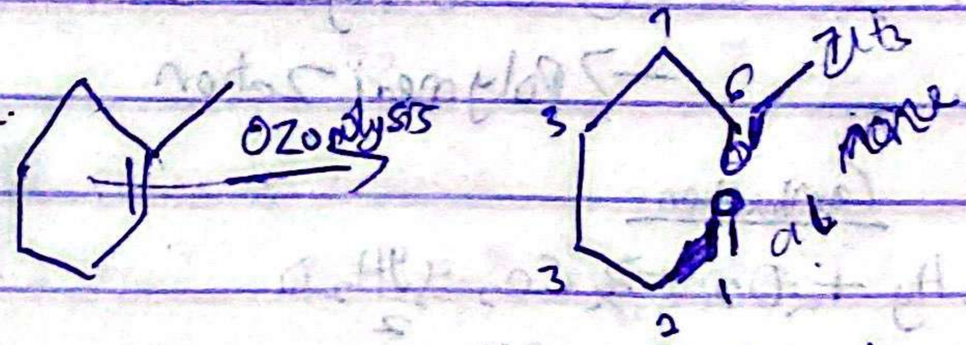
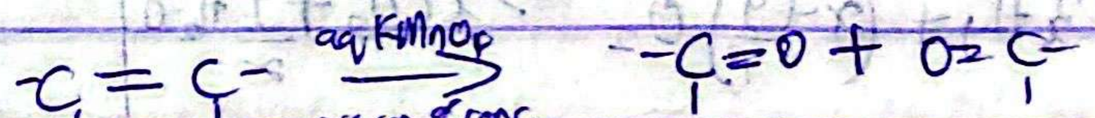


Note:

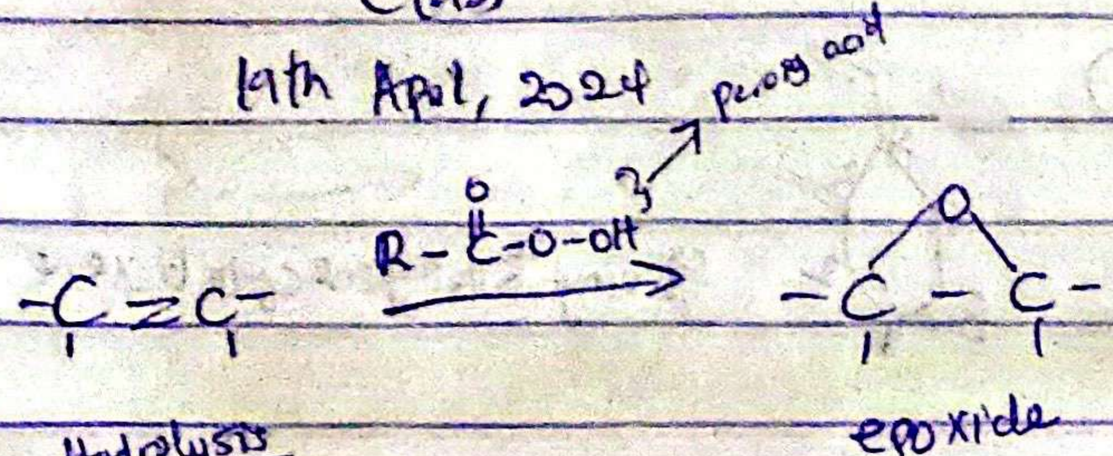
Note that OsO_4 can also be used



(iv)

Class

14th April, 2024



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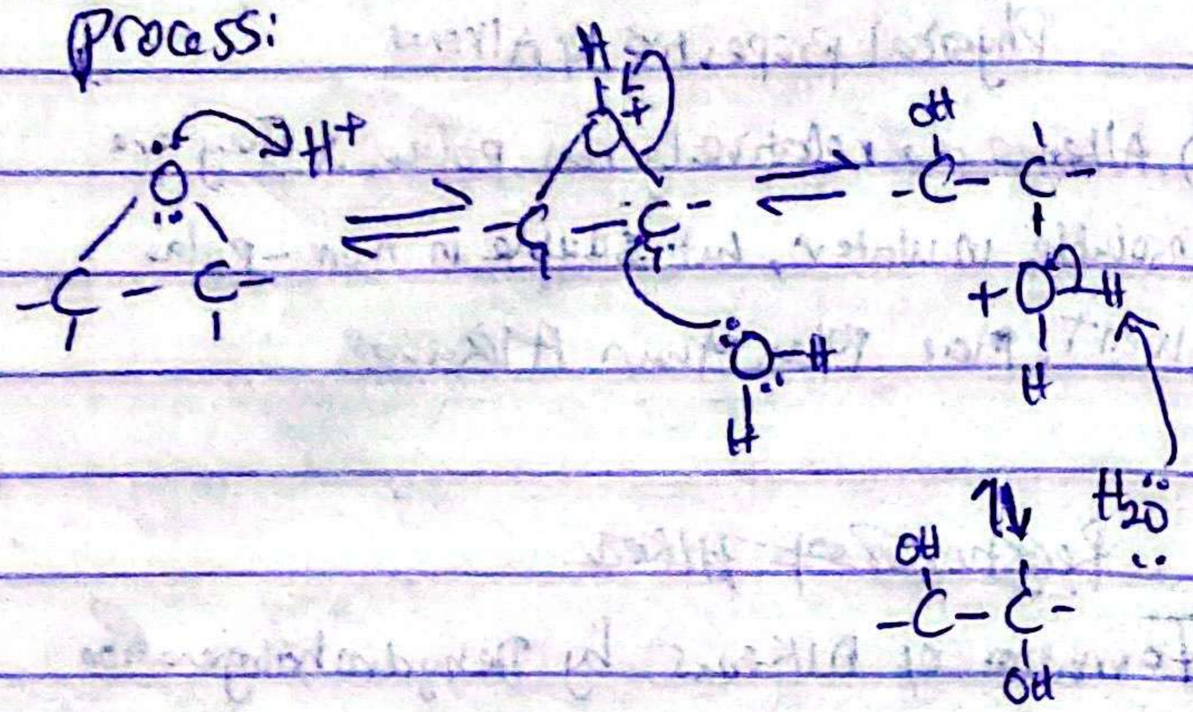
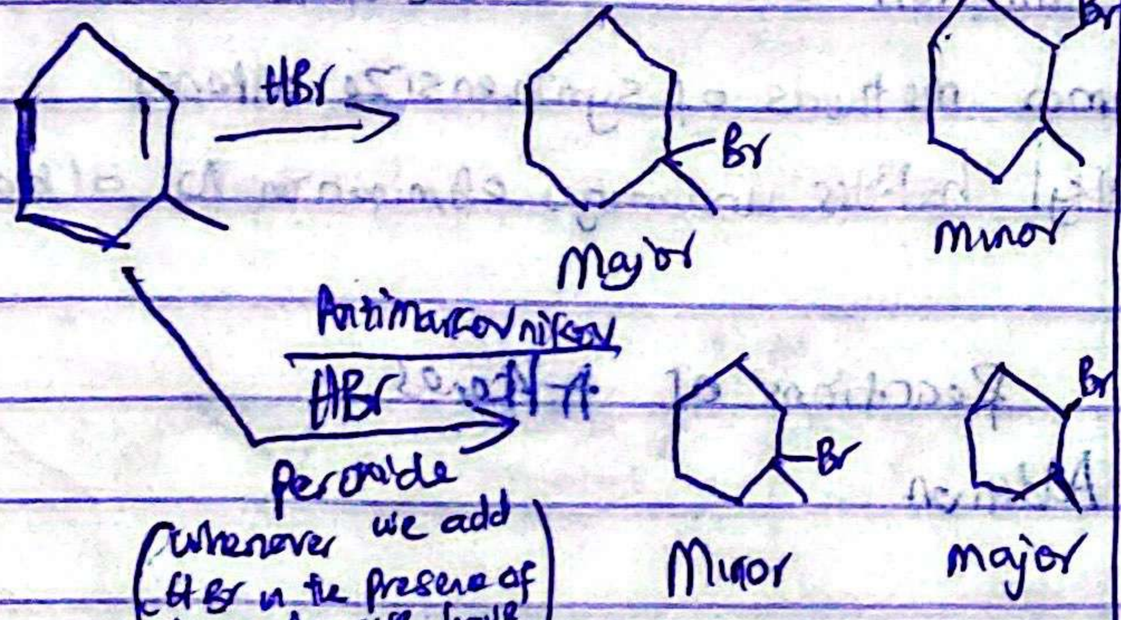
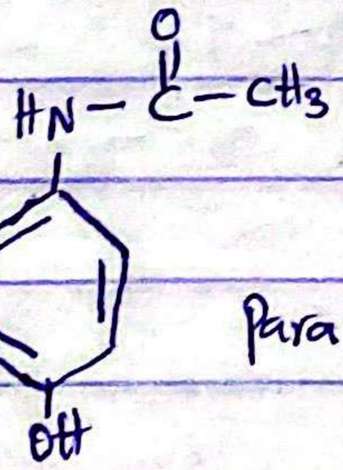
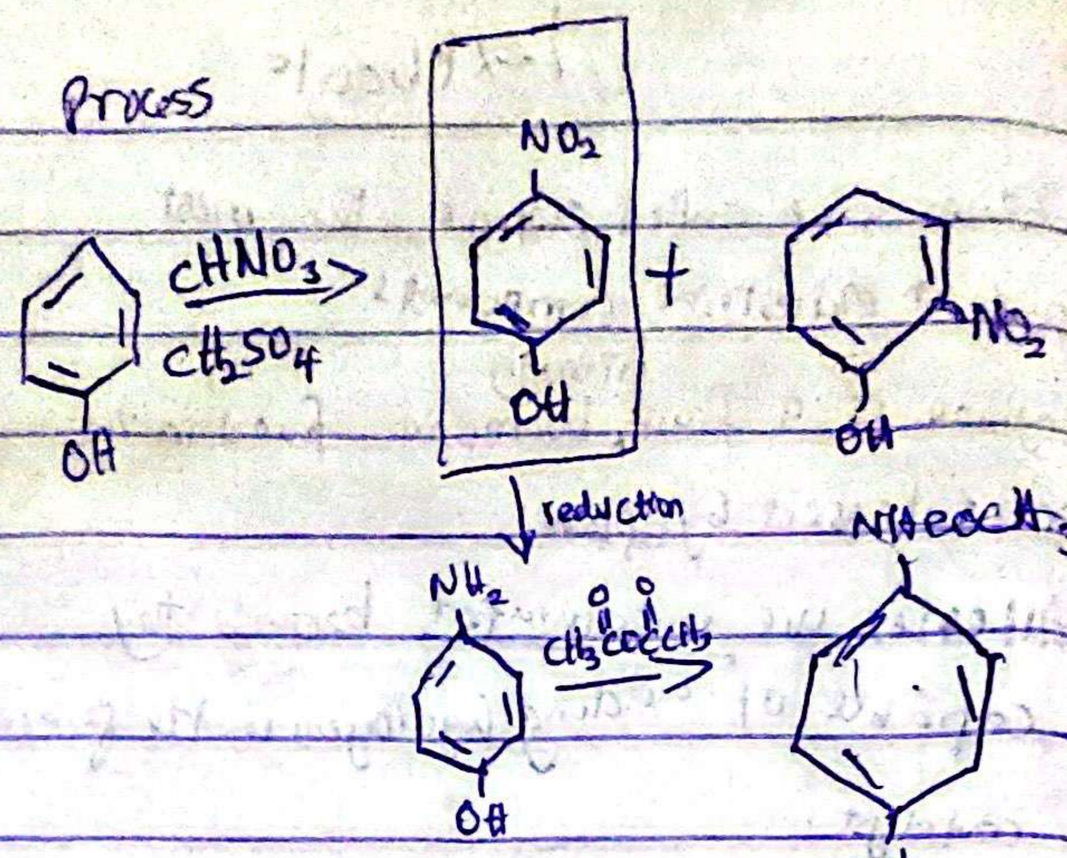


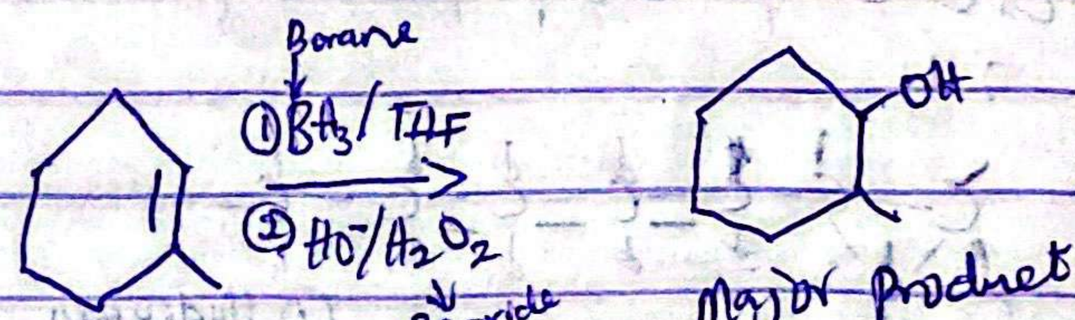




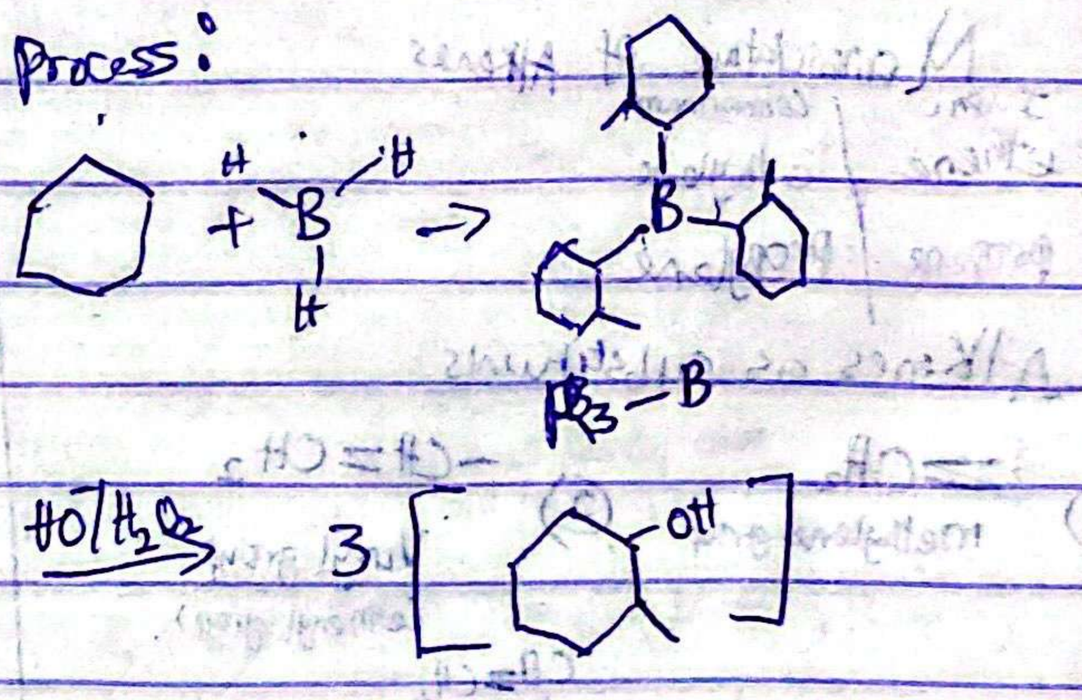
Process



Contd. of Anti Markovnikov



Process:

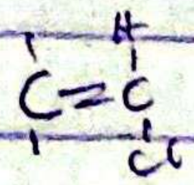


Polymerization of Alkenes

polyethene

Initiators stabilize ⊕ and ⊖

PVC

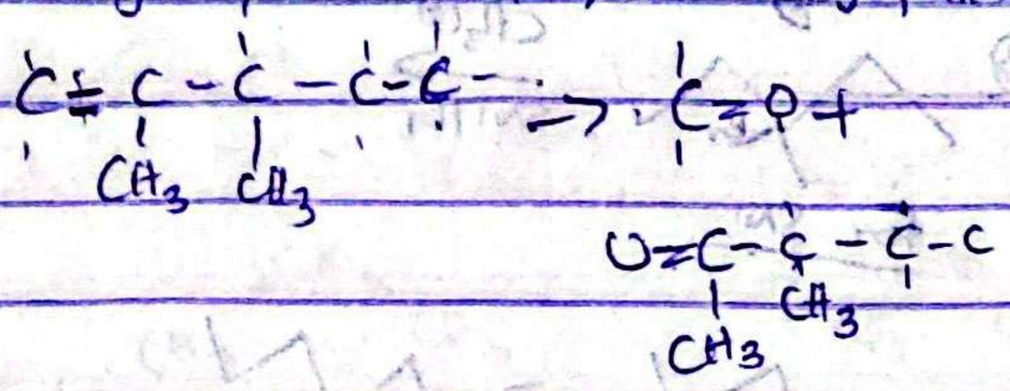


Vinyl chloride

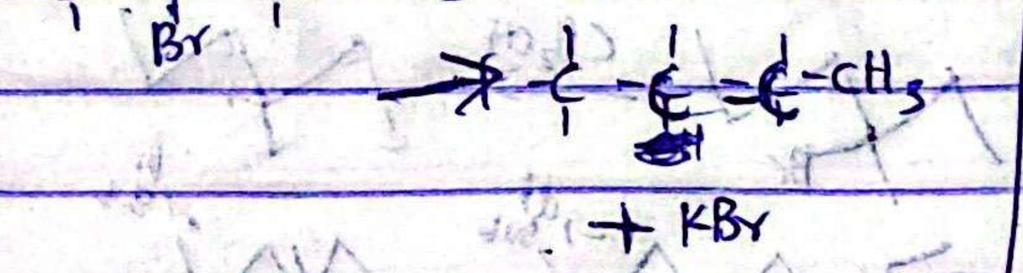
Styrene

Questions

(1) Ozonolysis products of 2, 3-dimethyl pentane



(2) Product when $CH_3CHBrCH_2CH_3$ reacts with KOH



Class

22nd April, 2024

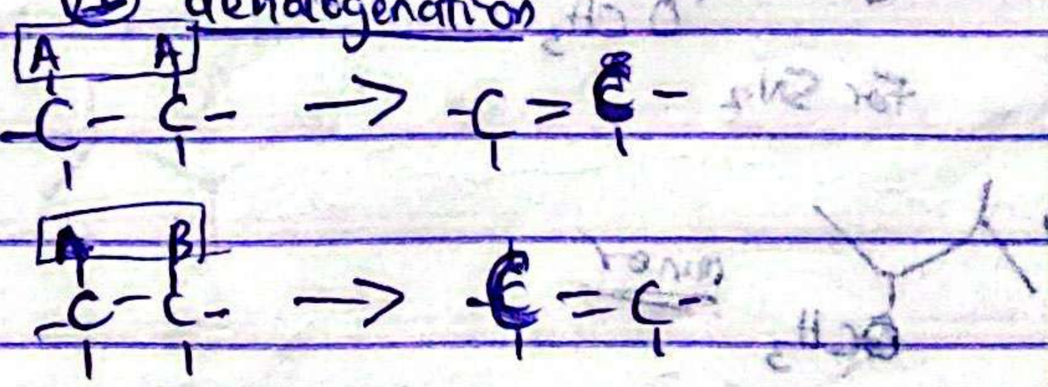
Preparation / Synthesis of Alkenes

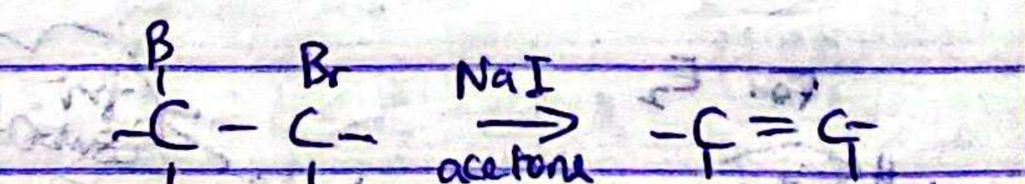
(1) dehydrohalogenation

(2) dehalogenation

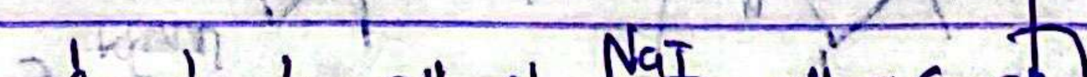
(3) dehydration

(A) dehalogenation

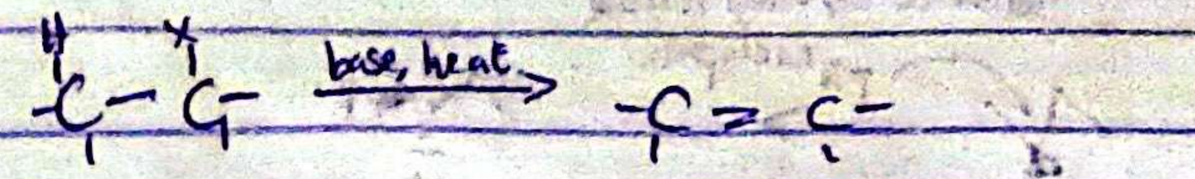




(i)

(ii) 

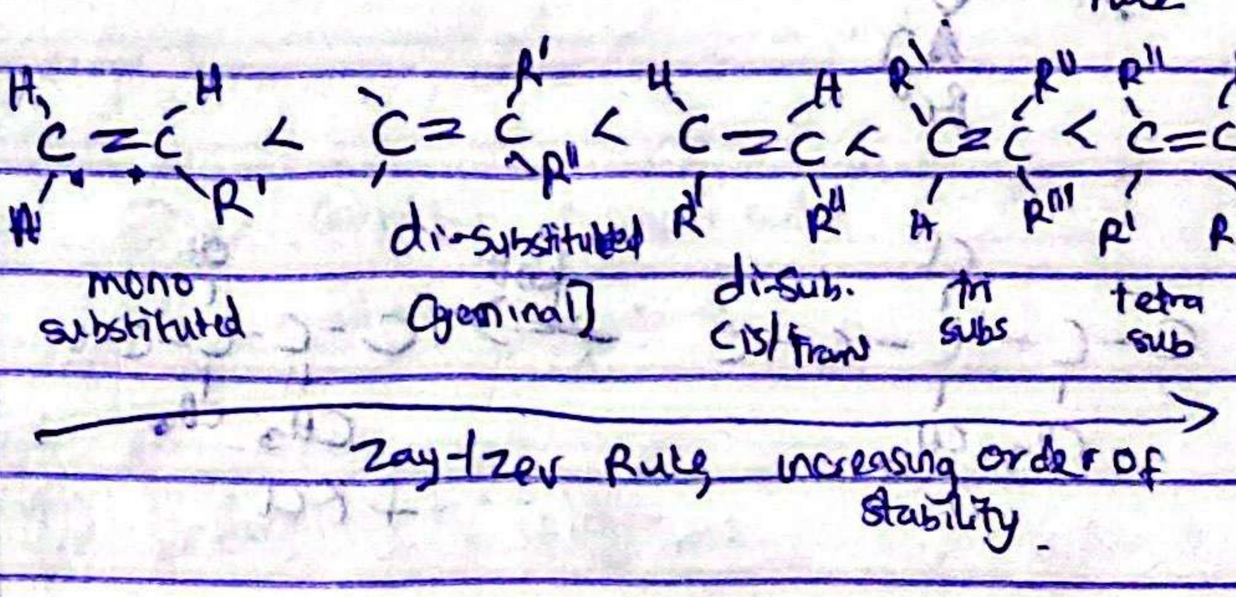
(2) dehydrohalogenation



Examples

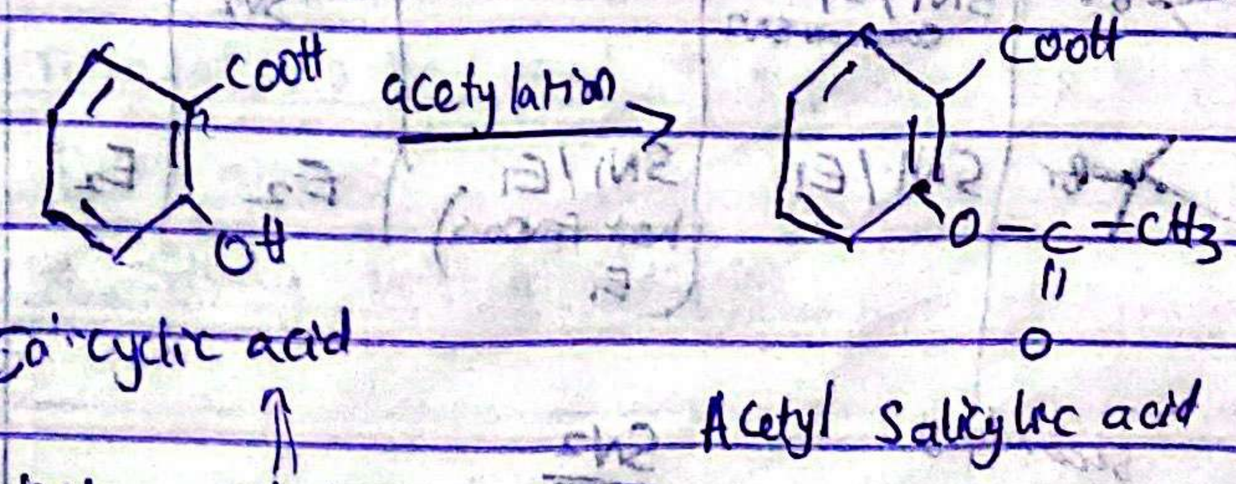
(i) $CH_3-CH_2-CH_2-Br \xrightarrow[heat]{CH_3O^-K^+} CH_3-CH=CH$ (methoxide)

(ii) $CH_3-CH(Br)-CH_2-CH_3 \xrightarrow[heat]{CH_3CH_2O^-K^+}$ $CH_2=CH-CH_2-CH_3$ minor and $CH_3-CH=CH-CH_3$ major product according to Zaytsev rule



Zaytzev Rule increasing order of stability.

(iii) $CH_3-C(CH_3)(CH_3)-CH(Br)-CH_3 \xrightarrow[\Delta]{CH_3O^-K^+}$ $CH_2=C(CH_3)-CH(CH_3)-CH_3$ minor and $CH_3-C(CH_3)=C(CH_3)-CH_3$ major



Salicylic acid

Kolbe-Schmidt reaction

Aspirin

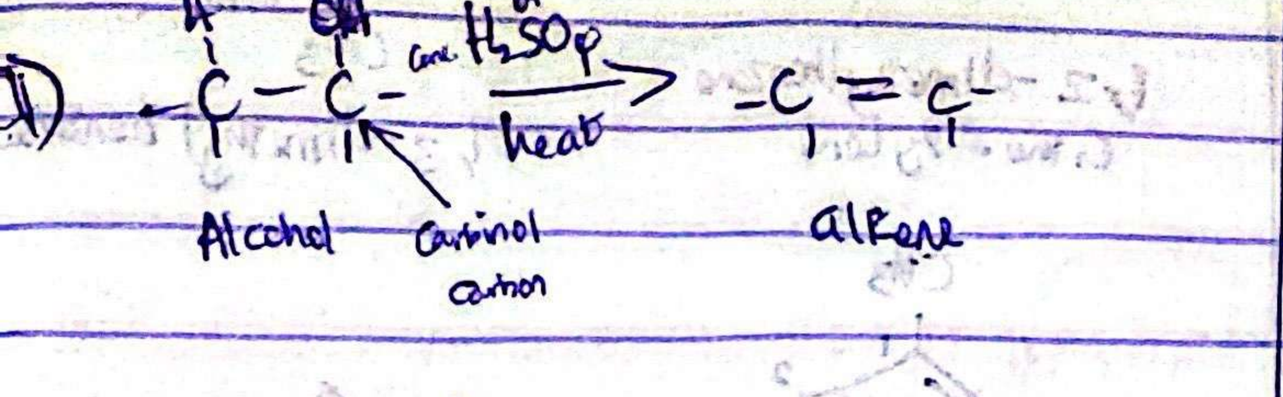
Acetyl Salicylic acid

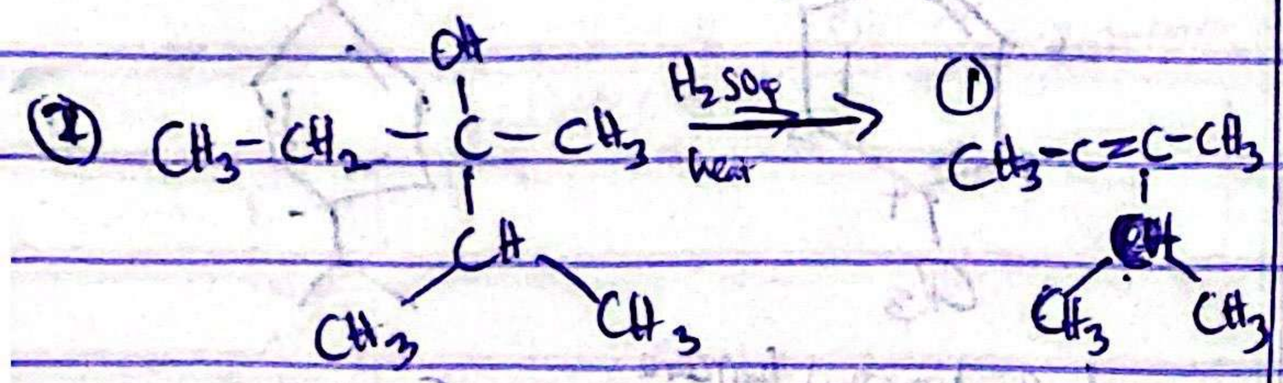
Class

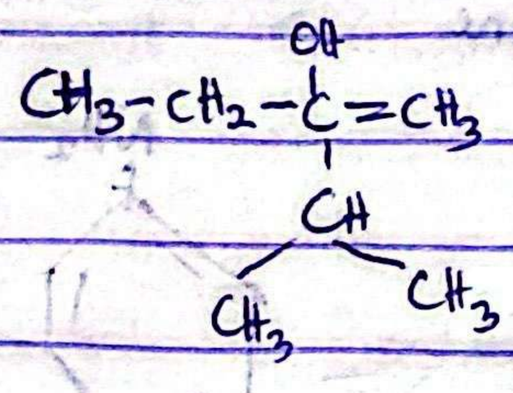
3rd April, 2024

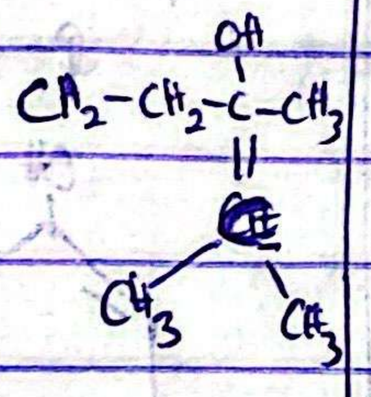
(*) At what temp will you get alkene and what temp will you get ether?

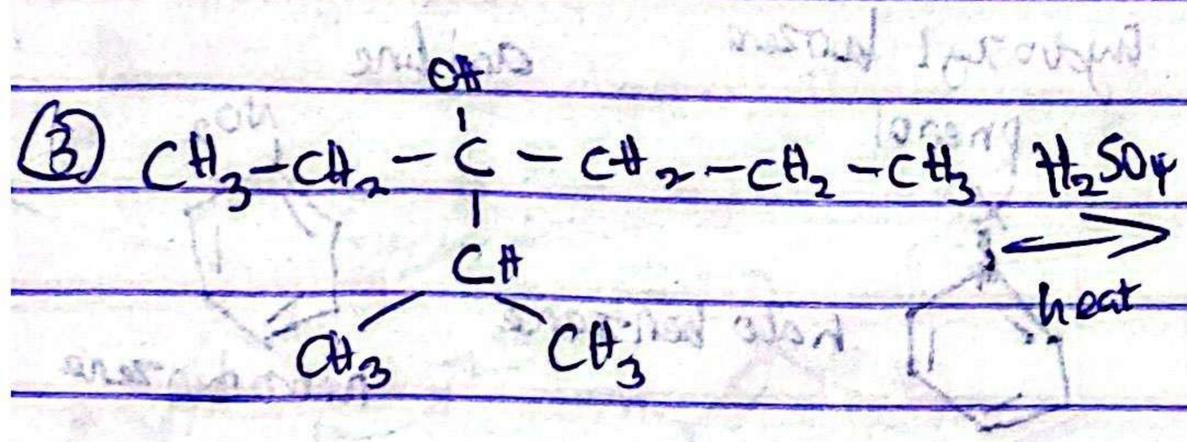
(3) Dehydration: Removal of water → Elimination

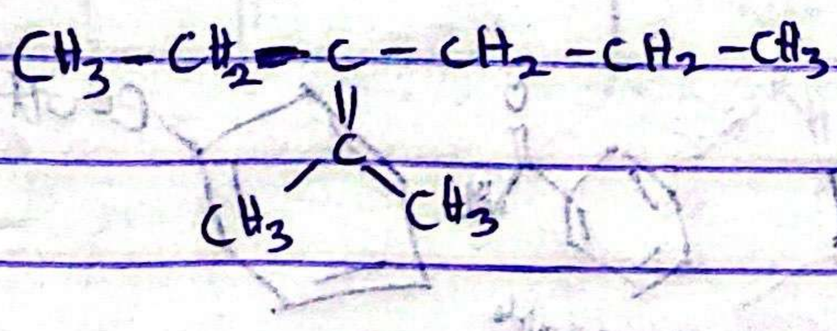
(1) 

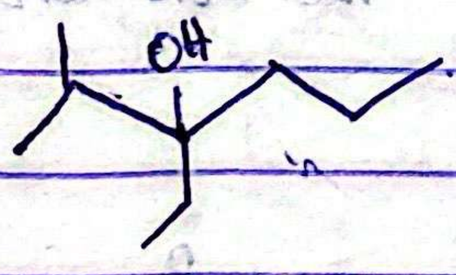
(1) 

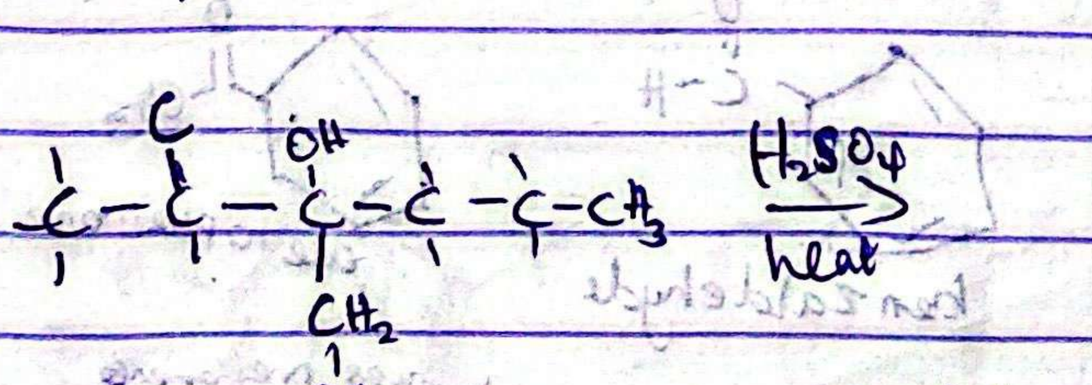
(2) 

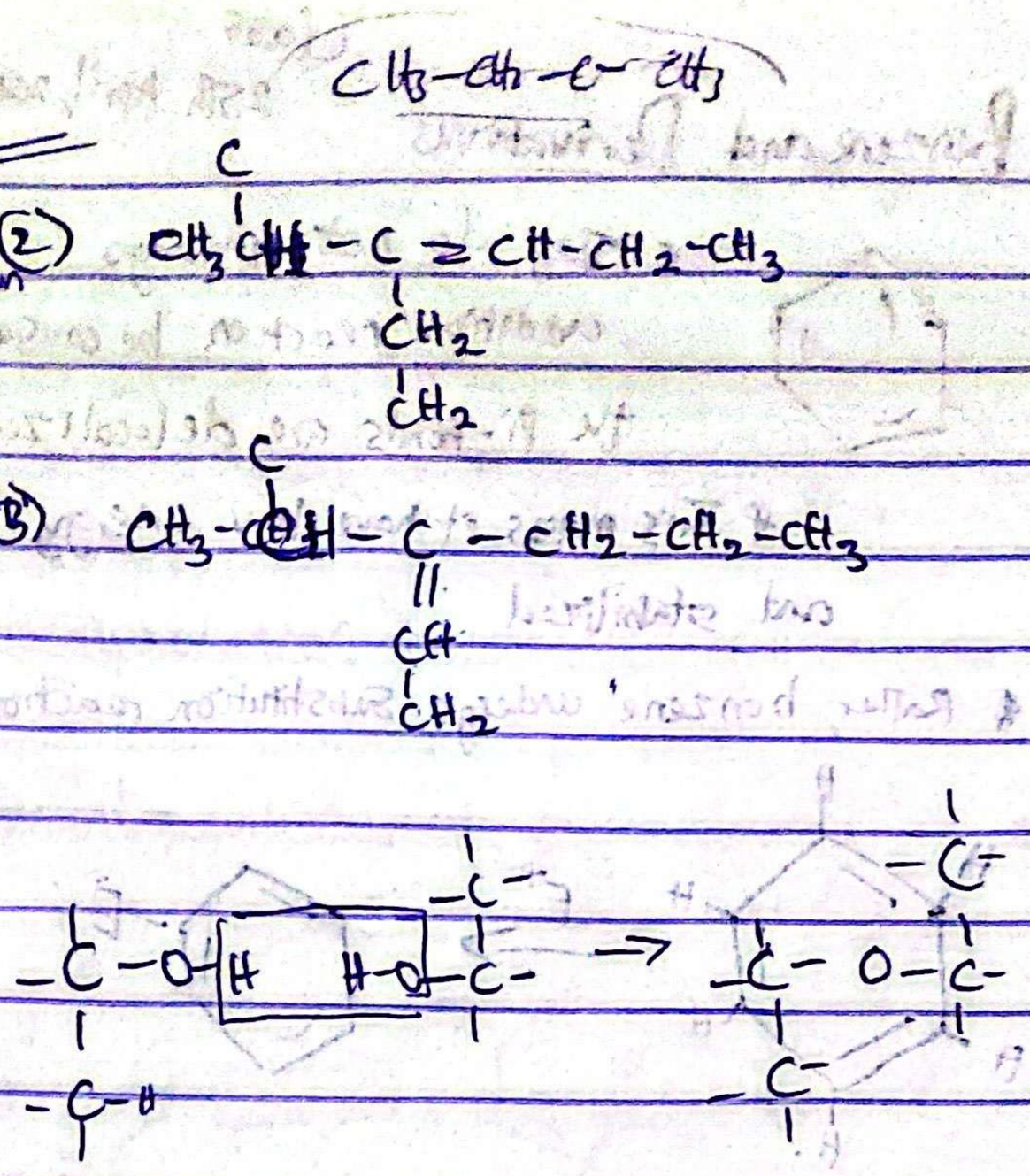
(3) 

(3) 





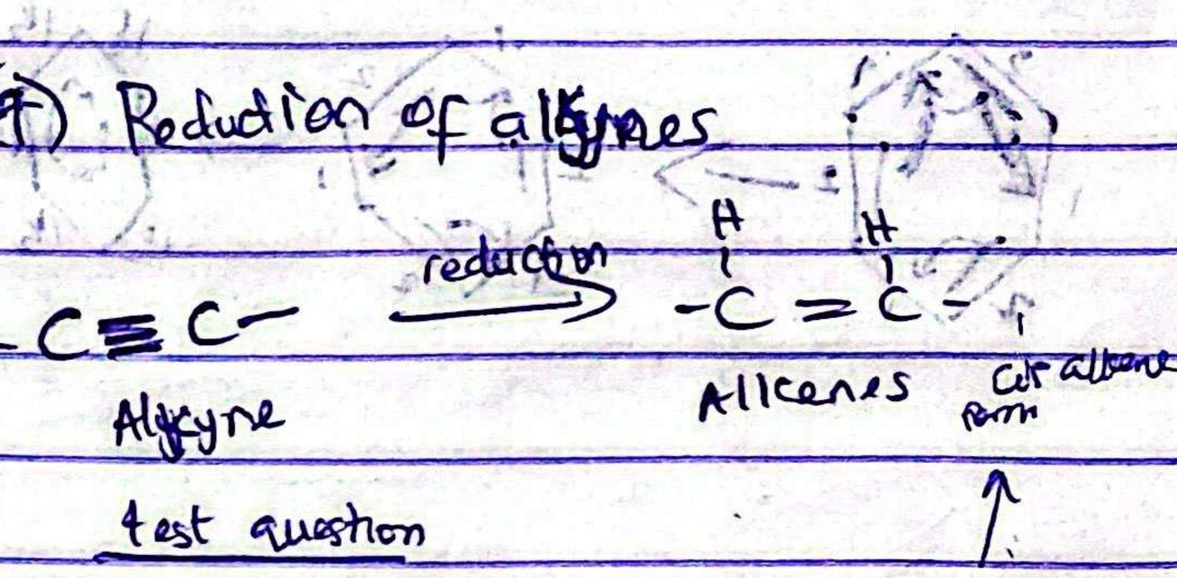




Ether can be formed under certain condition of temperature.

ether

(4) Reduction of alkynes



test question

* There are times that reduction of alkynes gives cis alkene or trans alkene, it depends on the reagent. Find out the reagent to be used to produce cis and trans alkenes.

* Study Wittig reaction

Stereochemistry of Alkenes

* Cahn-Ingold-Prelog Convention

↓ Cis alkene is formed when Pd/BaSO4 in the presence of quinoline is used as reagent

Trans alkene is formed when Na and liq NH3 is used as reagents

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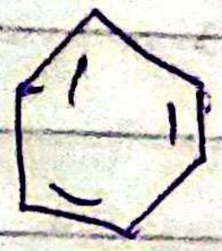
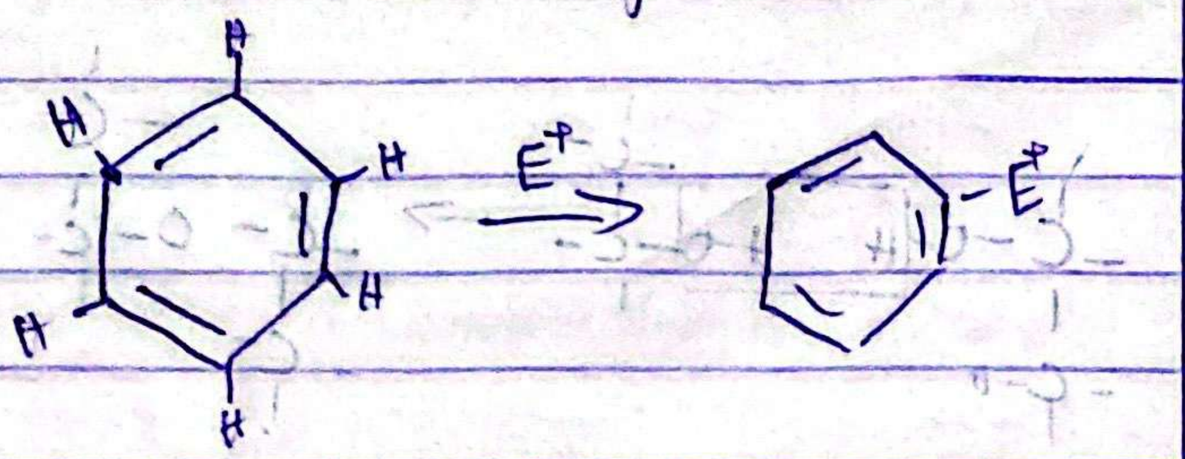
Class

25th April, 2024

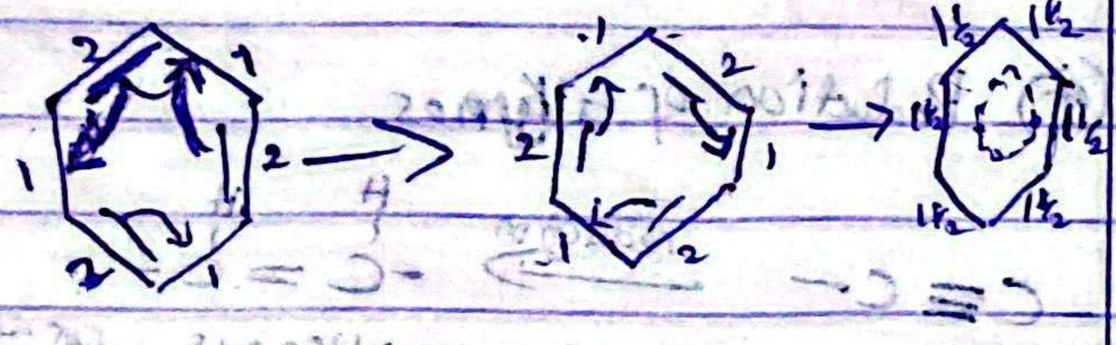
Benzene and Derivatives



* They do not undergo addition reaction because the Pi-Bonds are delocalized
* This makes it have low energy and stabilized
* Rather, benzene undergo Substitution reaction

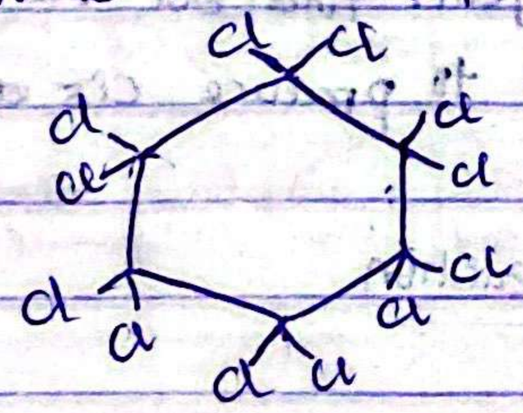


* The double bond are not really really, they are pseudo

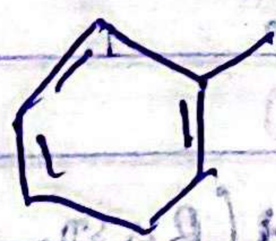


25th April, 2024

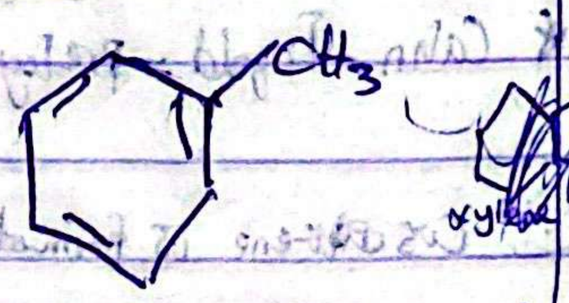
Benzene Undergo addition reaction but it is not normal



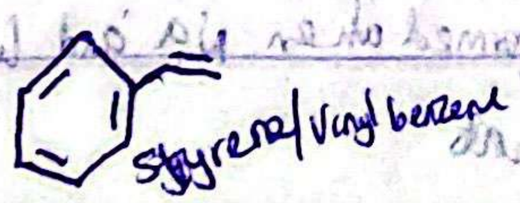
Derivatives of Benzene and Nomenclature



Alkyl benzene



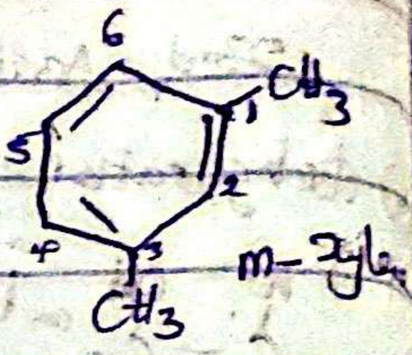
methyl benzene
Toluene



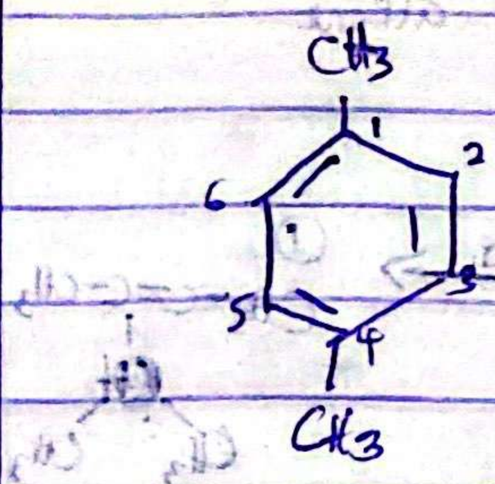
styrene/vinyl benzene

O = ortho, m = meta, P = Para

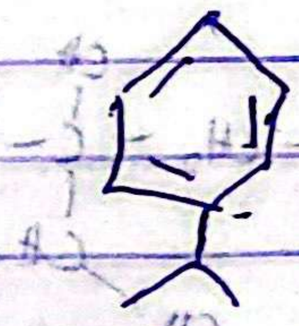
1,2-dimethylbenzene
Ortho-xylene



m-xylene
1,3-dimethyl benzene

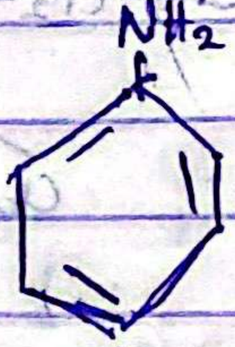


1,4-dimethyl benzene
P-xylene

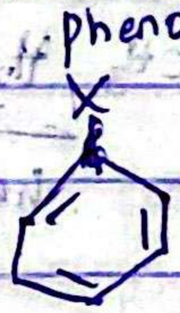


Cumene

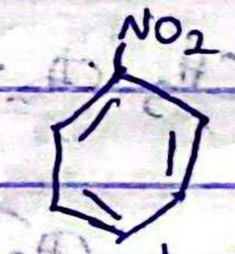
Hydroxyl benzene
phenol



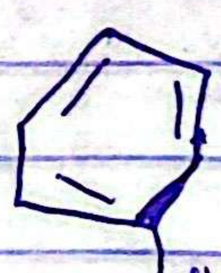
aniline



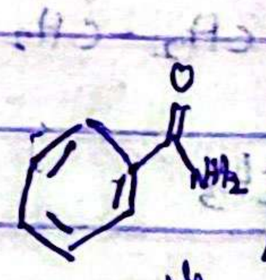
halo benzene



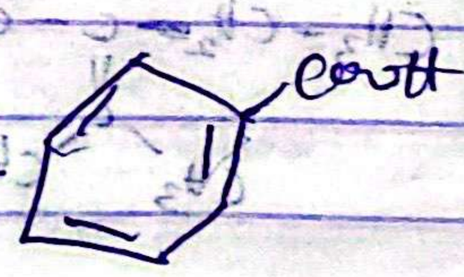
nitrobenzene



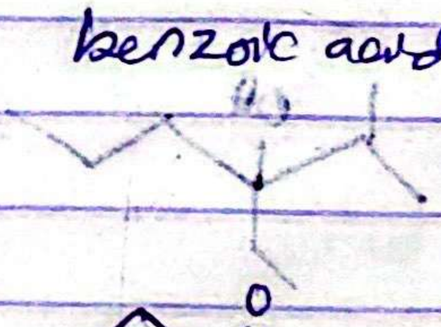
methoxy benzene
Anisole

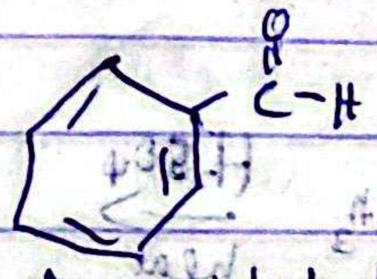


Benzamide

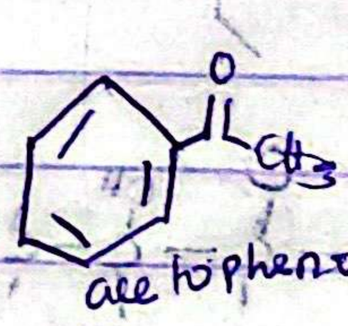


benzoic acid

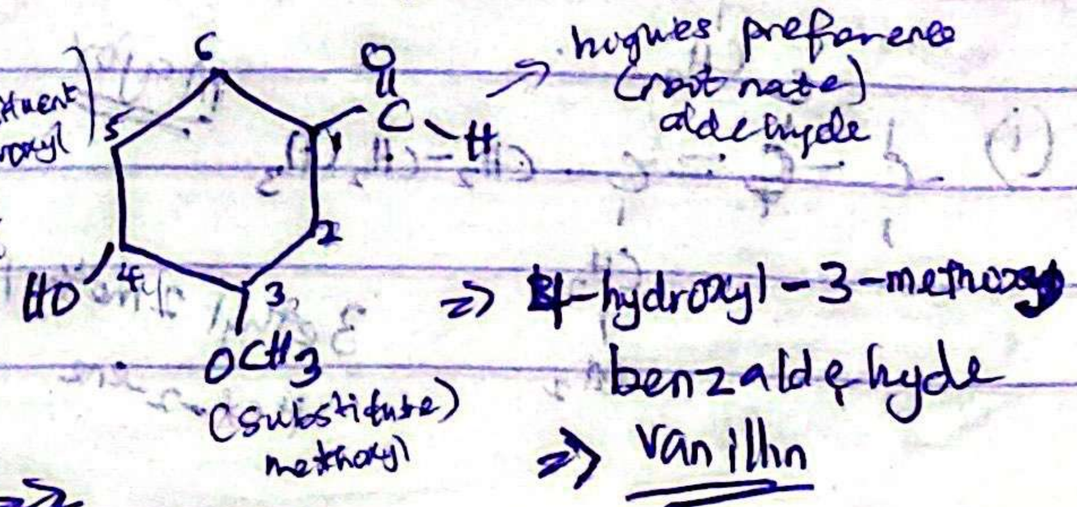




benzaldehyde



acetophenone

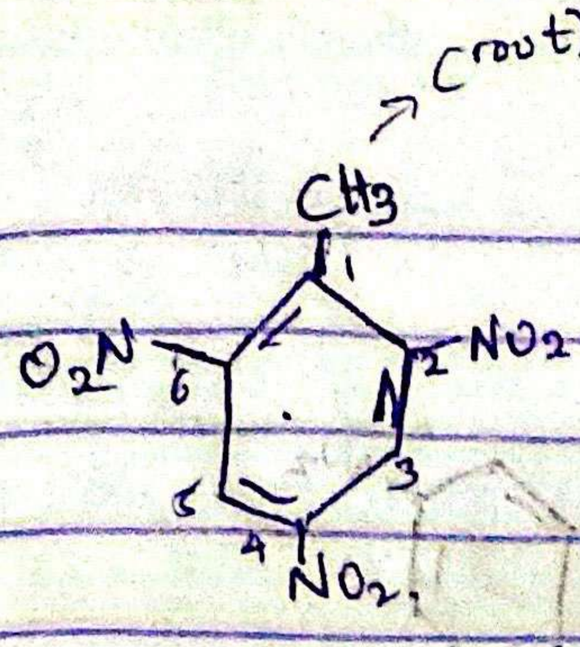


Substituent (oxygen)

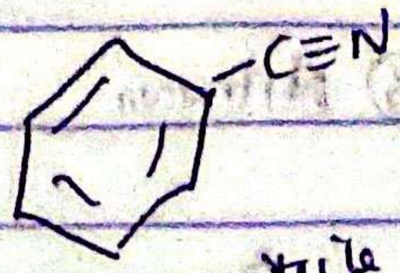
Hugues preference (root name) aldehyde

4-hydroxyl-3-methoxy benzaldehyde

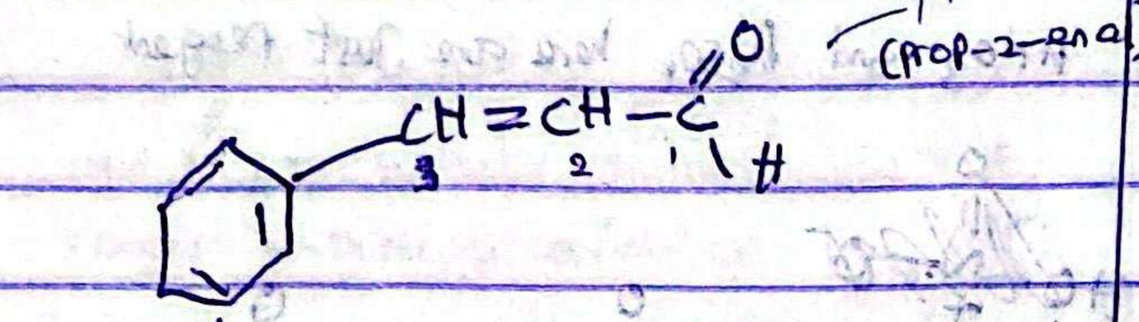
⇒ Vanillin



2, 4, 6-trinitro toluene



Benzonitrile

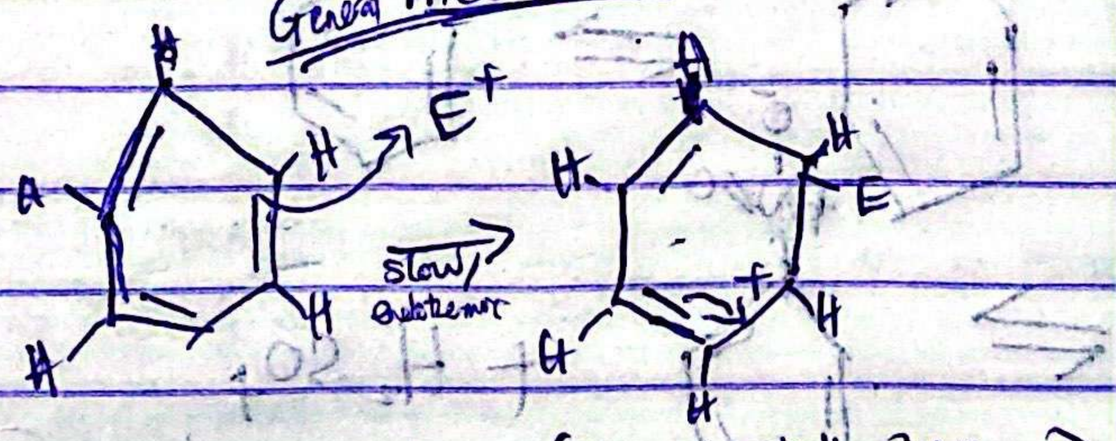


3 phenyl prop-2-enal
Cinnamaldehyde

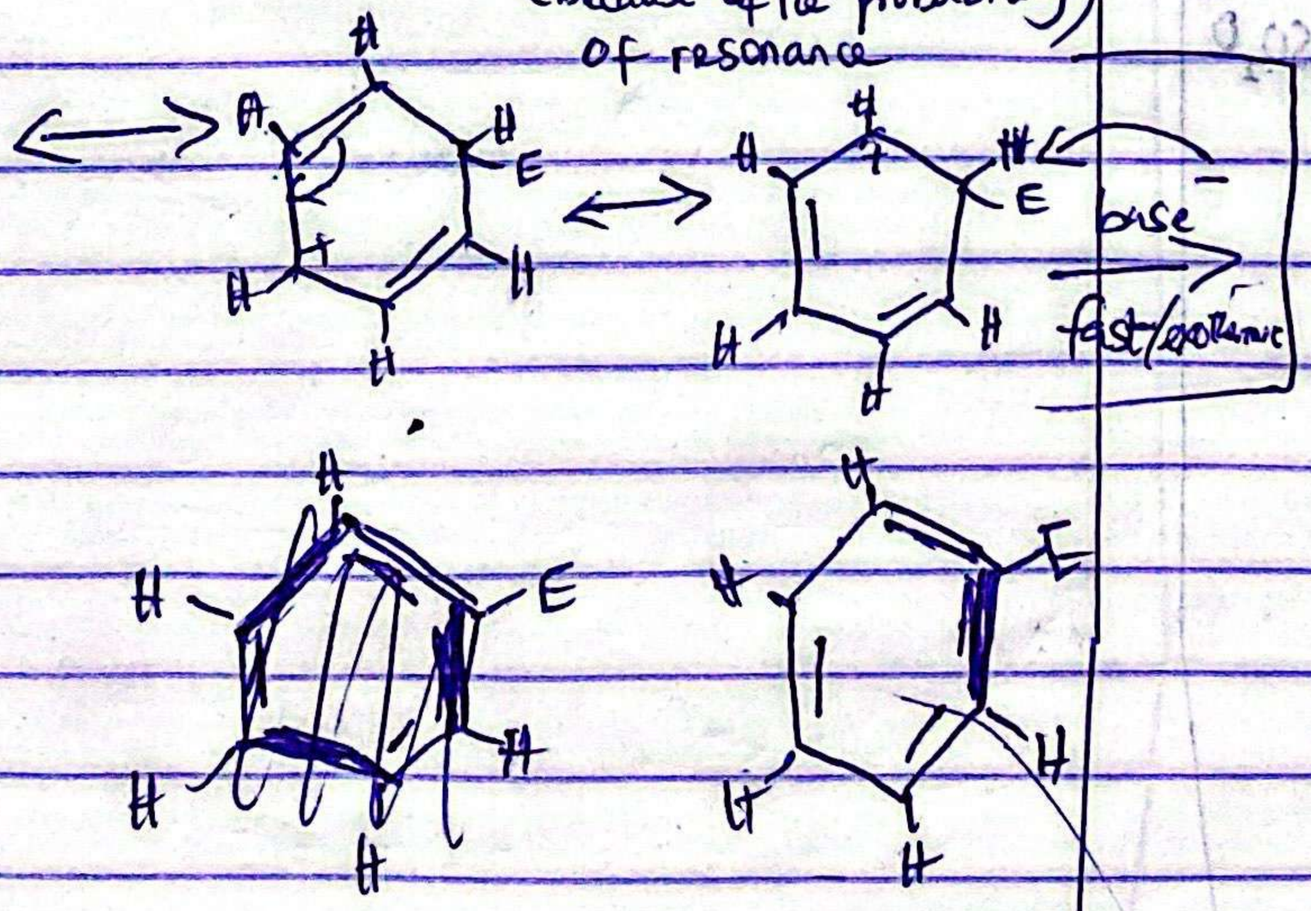
Reactions of Benzene

(1) Electrophilic substitution reaction:
Benzene is as nucleophile, having 6 Pi electron.

General mechanism



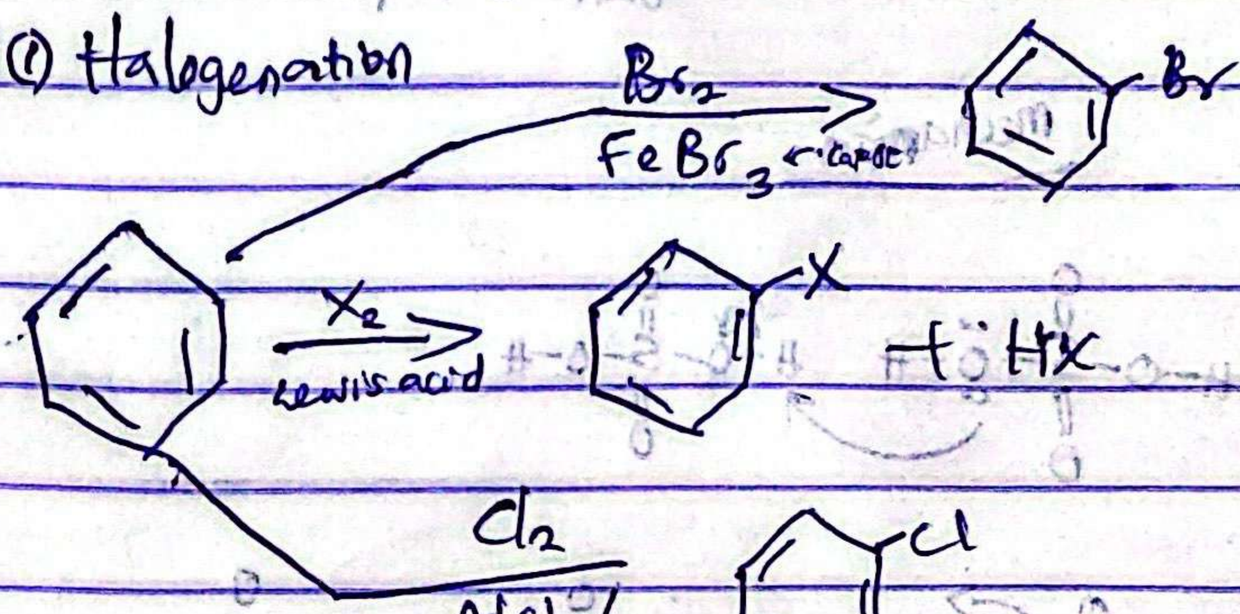
(This not really stable because of the probability of resonance)



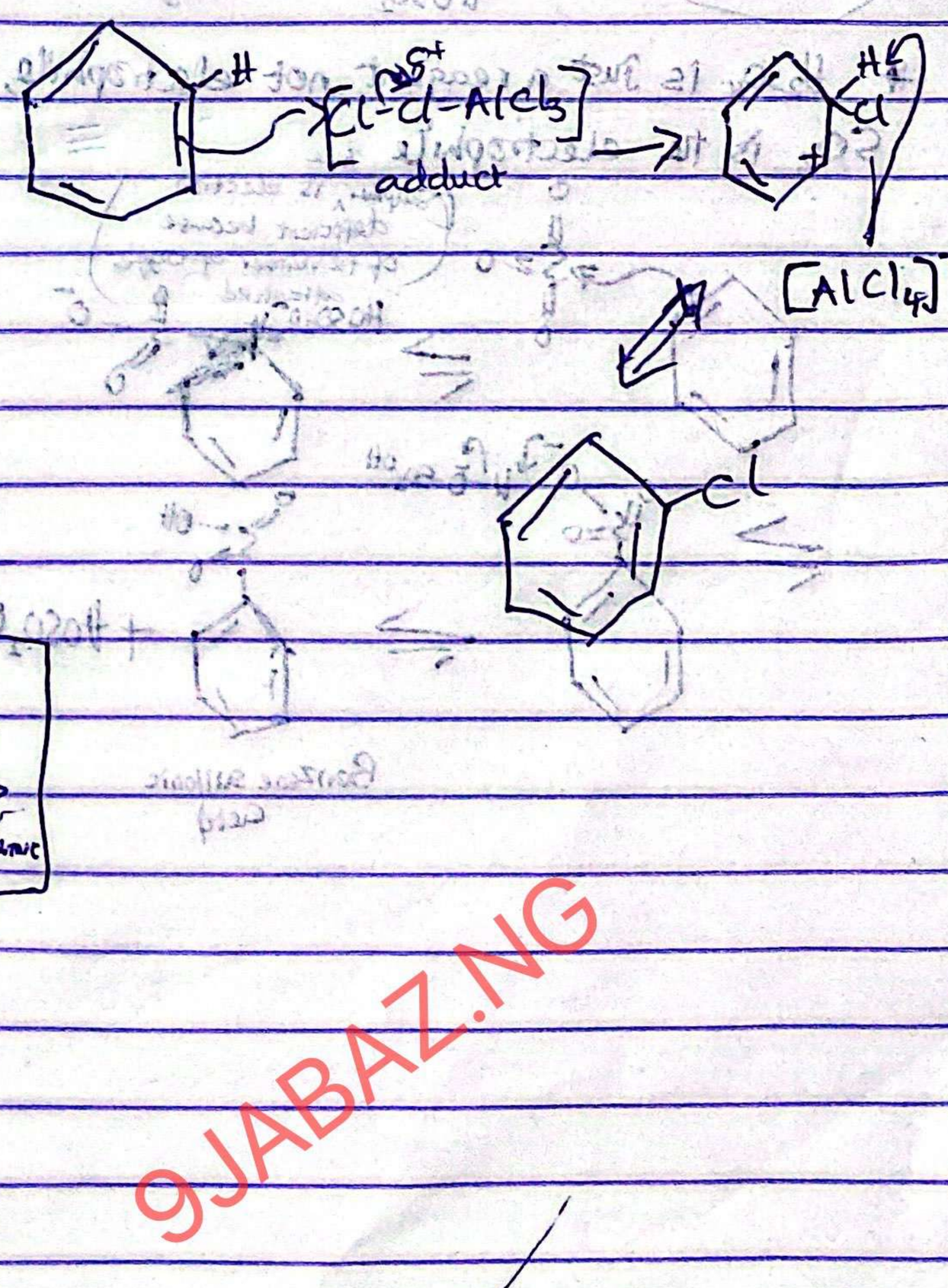
4 hydroxy 3 one

Halogenation
Alkylation (Friedel-Crafts)
Acylation (Friedel-Crafts)
Nitration
Sulphonation

(1) Halogenation



Mechanism:

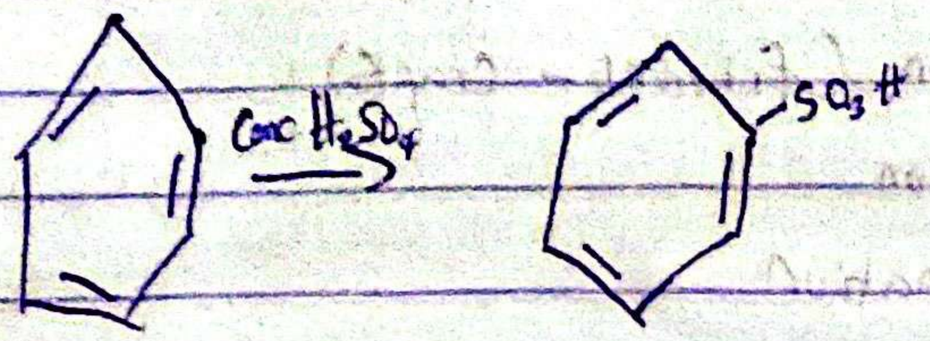


9JABAZ.NG

Class

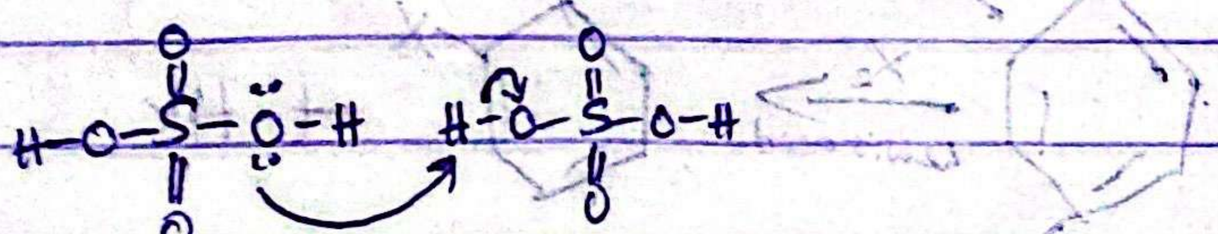
26th April, 2024

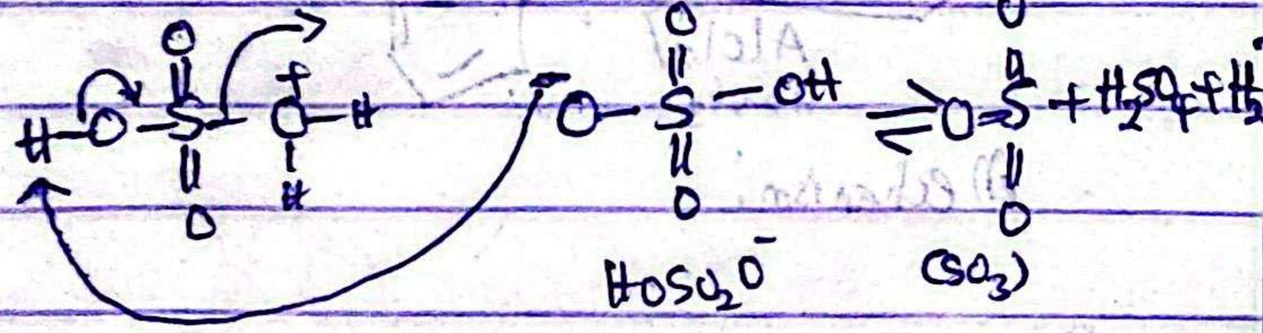
② Sulphonation



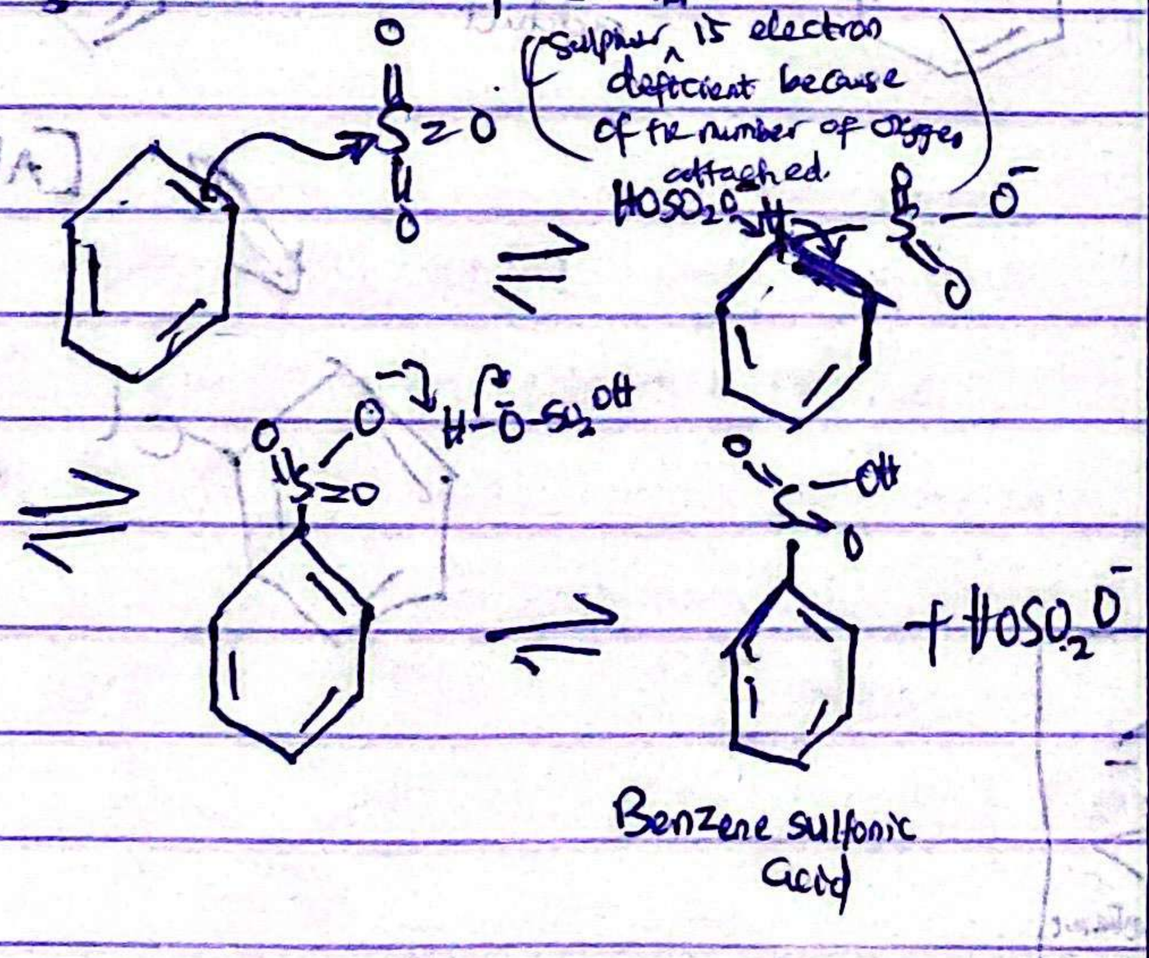
Benzene Sulfonic acid

Mechanism



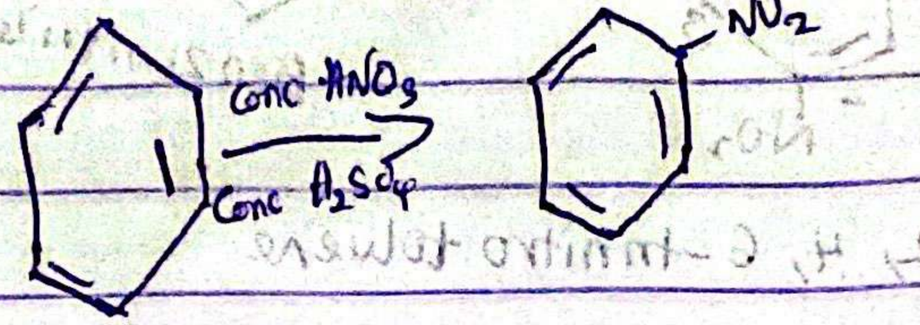


* H_2SO_4 is just a reagent not electrophile, SO_3 is the electrophile



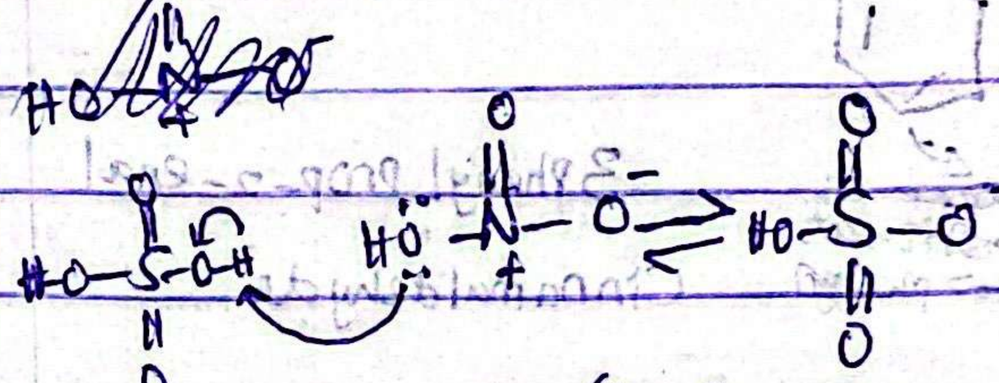
Benzene sulfonic acid

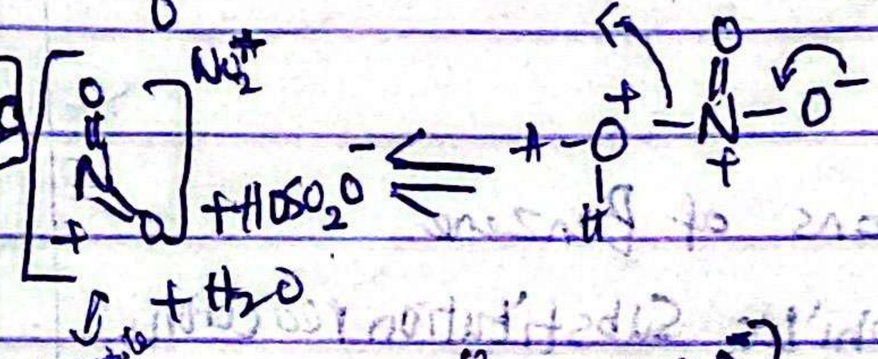
③ Nitration

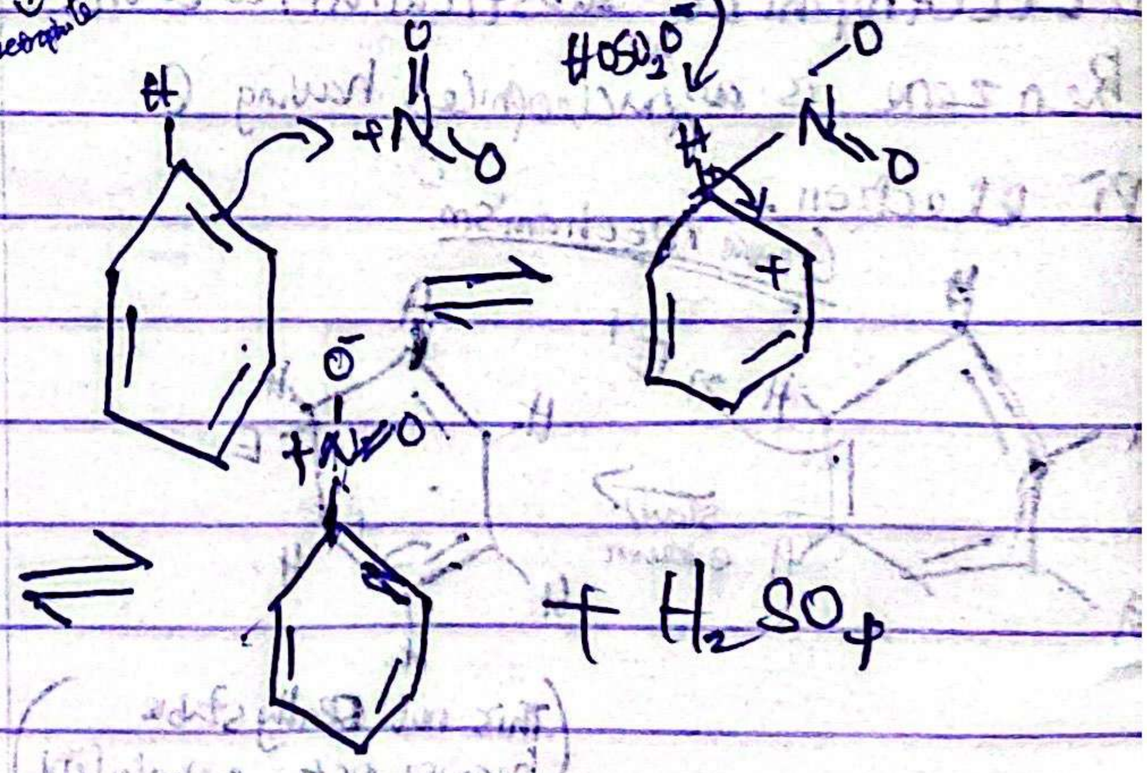


Mechanism

HNO_3 and H_2SO_4 here are just reagent

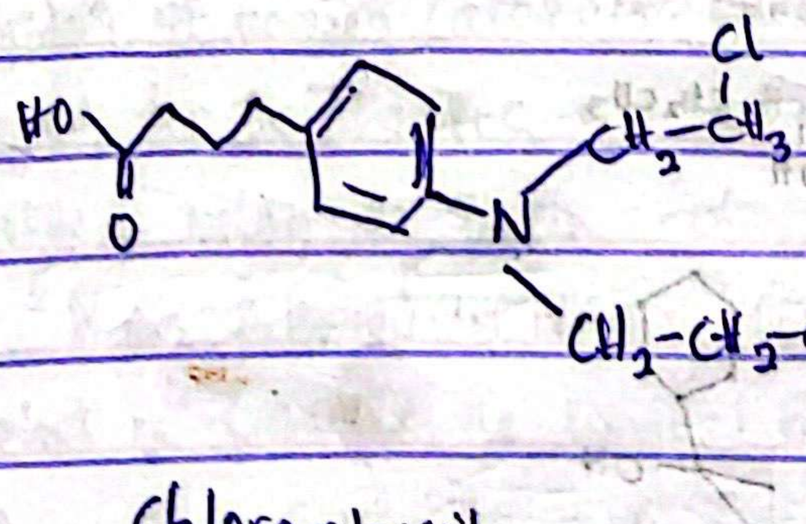






Cor

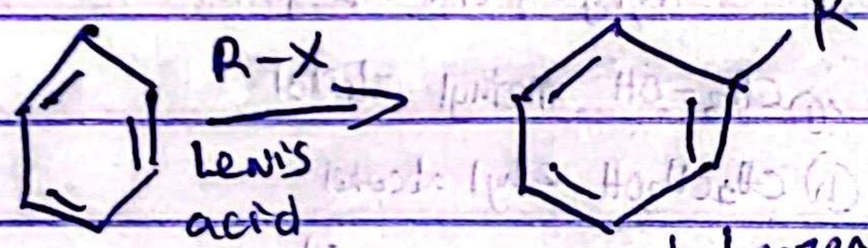
Why organic Chemistry is important



Chlorambucil

used in cancer patients. It undergoes SN2 reaction with the DNA/purine.

(4) Friedal-crafts Alkylation



Mechanism

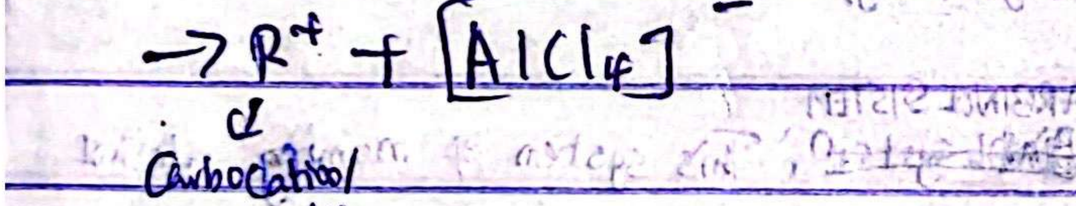
$R-Cl + AlCl_3 \rightarrow [R^{\delta+}-Cl-AlCl_3]$

$\rightarrow R^+ + [AlCl_4]^-$

Carbocation/electrophile

If $R = CH_3$ or CH_3CH_2, it will not form a carbocation, it will be unstable

* An hydride shift



24th April 2024

Hydroxyl Compounds

Hydroxyl compounds are compounds with one or more hydroxyl functional groups (-OH) attached to a saturated carbon atom.

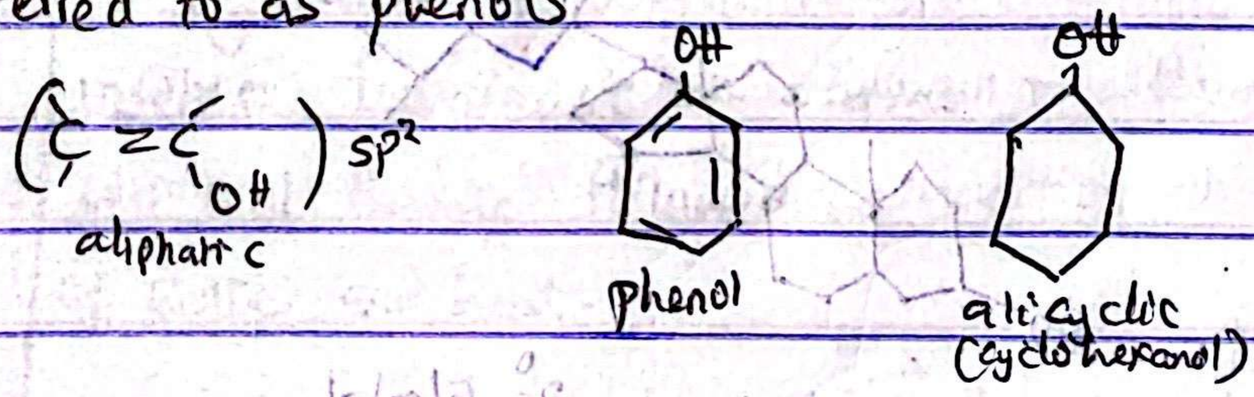
The Saturated carbon atom or a simple alkyl group

Alkanols (Alcohols)

Alkanol are hydroxyl compounds of general formular of R-OH. The -OH group is attached or bonded to a saturated carbon atom (Sp^3)

$-\overset{|}{C}-OH$ Sp^3

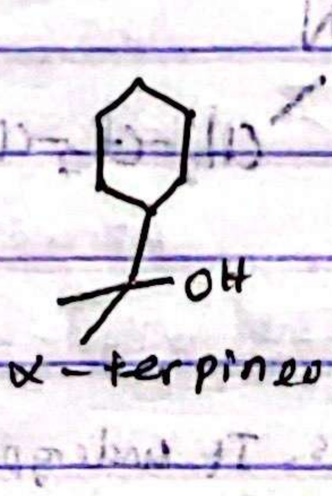
While there are some in which OH will attach to sp^2 hydridized carbon. Carbon in which their OH group is attached to Vinylic sp^2 is called "enol" while those in which the -OH is bonded to a benzene ring are referred to as phenols



However enols and phenols behave differently from alcohols

Classification

Alkanols are classified into 3 on the basis of which the OH group is bonded or attached to.

Class	Gen. Formular	Functional group	Examples
must have 2 hydrogen	1°	$R-CH_2-OH$	$-CH_2OH$	$H-CH_2-OH$, CH_3CH_2OH
must have two hydrogen and 2 alkyl group	2°	$R-\underset{OH}{\underset{\vert}{CH}}-R'$	$-\underset{OH}{\underset{\vert}{CH}}-$	$CH_3\underset{OH}{\underset{\vert}{C}}H-CH_3$, $CH_3-\underset{OH}{\underset{\vert}{CH}}-CH_2CH_3$
NO hydrogen, 3 alkyl group	3°	$R-\underset{OH}{\overset{R'}{\overset{\vert}{\underset{\vert}{C}}}}-R''$	$\rangle\!\!-OH$	$CH_3-\underset{OH}{\overset{CH_3}{\overset{\vert}{\underset{\vert}{C}}}}-CH_3$, 

α-terpineol

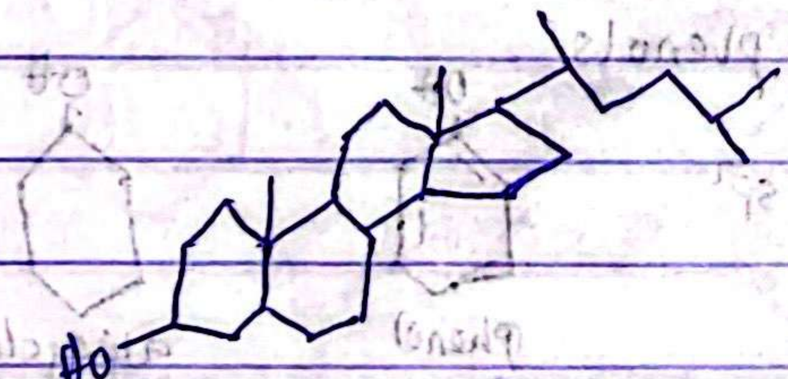
Alcohols can be further classified on the basis of the number of hydroxyl group per molecule or attached to different carbon atoms:

(1) Monohydric: contain only one -OH per molecule

(2) Dihydric: contains two -OH per molecule. The simplest form is Ethane-1-2-diol. (glycol)

$CH_2(OH)-CH_2(OH)$ common name

Example of 2°



Cholesterol 2° alcohol

(3) Trihydric: contains 3-OH per molecule

Example: Propan-1,2,3-triol (glycerol)

$CH_2(OH)-CH(OH)-CH_2(OH)$

(4) Polyhydric: More than 3 or many -OH per molecule

Nomenclature

There are three important system used in name alcohols:

(1) Use of common names (systems) or functional class system

This is good for simple alkanols

How? Name the alkyl group (R) and follow the word alcohol

Example: (i) CH_3-OH methyl alcohol

(ii) CH_3CH_2OH ethyl alcohol

(iii) $CH_3-\underset{CH_3}{CH}-OH$ iso propyl alcohol

(iv) $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{\vert}{C}}}-CH_3$ tet-butyl alcohol (t-butyl alcohol)

(v) $CH_3-\underset{OH}{CH}-CH_2CH_2CH_2CH_3$.

methyl Pentyl alcohol

(2) CARBINOL SYSTEM

~~Carbinol system~~: This system of naming alcohol considers all alcohols to have been derived from methyl alcohol by the replacement of one or more hydrogen atom by other groups: RULES:

(1) Name the group(s) attached to the carbon bearing the -OH group and then add the suffix carbinol to depict the -OH portion. Example:

(i) $CH_3CH_2CH_2-\underset{H}{\overset{H}{\underset{\vert}{C}}}-OH$

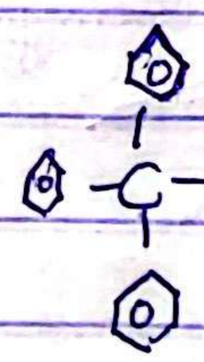
propyl carbinol

(ii) $CH_3CH_2-\underset{H}{\overset{H}{\underset{\vert}{C}}}-OH$

ethyl carbinol

(iii) $CH_3CH_2-\underset{CH_2CH_3}{\overset{H}{\underset{\vert}{C}}}-OH$

diethyl carbinol

(iv) 

Triphenyl carbinol

30th April, 2024

(3) IUPAC SYSTEM: This is the most versatile system of naming alcohols. Simple alcohols are named by the IUPAC as derivatives of parent alkane using the suffix -ol.

Rules Followed in Naming Using IUPAC

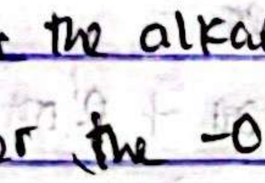
1) Select or consider the longest, or continuous carbon chain containing the -OH group in deriving the parent name

2) Number the alkane chain, begining and the end nearer the -OH group so as to give carbon atom to which the -OH functional group is attached the lowest possible numbers

Examples

(1) $CH_3CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH$ (4, 3, 2, 1)

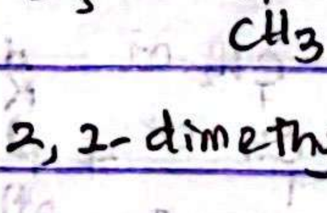
2, 2-dimethyl butanol

(2)  $-CH_2CH_2OH$

2 phenyl ethanol

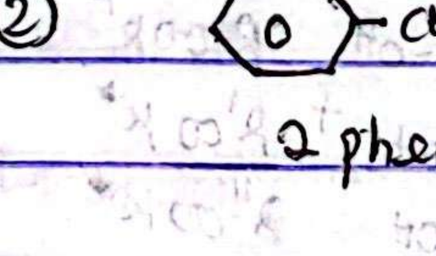
(3) $-OH$

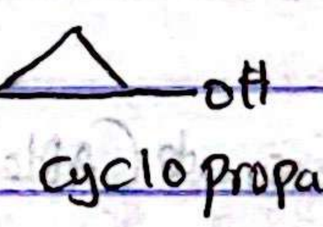
cyclopropanol

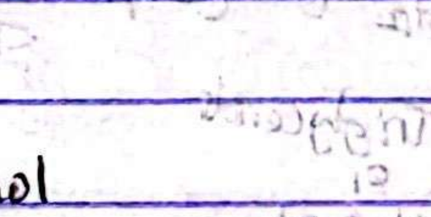
(4)  $-OH$, $-CH_3$, $-CH_3$

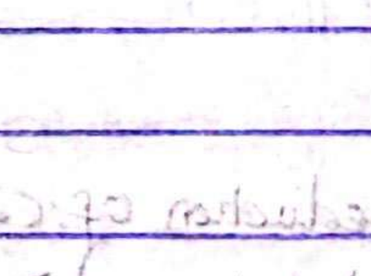
2, 3-dimethylcyclooctanol

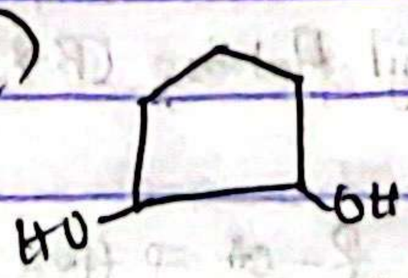
Questions

(1) 

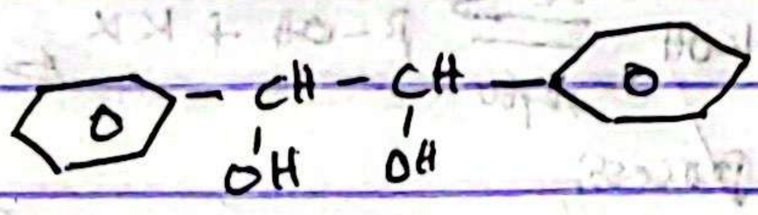
(2) 

(3) 

(4) 

(5) 

(6) $CH_3-\overset{OH}{\underset{}{C}}=\overset{CH_3}{\underset{}{C}}-\underset{CH_3}{CH}-CH_3$

(7) 

Physical Properties of Alkanols:

(1) Alkanols have high boiling points at room temperature

(2) They are miscible or soluble in water

All these physical properties can be explained in terms of intermolecular hydrogen bond

(3) Preparations of Alkanols

(1) Hydration of Olefins/Alkenes: This involves treatment of olefins or alkenes with cold H_2SO_4 followed by addition of water and heat.

(i) $\overset{}{C}=\overset{}{C} + H_2SO_{4(aq)} \longrightarrow H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OSO_3H}{C}}-H$

$\xrightarrow[\Delta]{H_2O} -\overset{}{C}-\overset{}{\underset{OH}{C}}- + H_2SO_4$

(ii) $CH_3CH=CH_2 \xrightarrow{80\%\ H_2SO_4} CH_3-\underset{OSO_3H}{CH}-CH_3$

$\xrightarrow[\Delta]{H_2O} CH_3-\underset{OH}{CH}-CH_3 + H_2SO_4$

② Hydrolysis of Alkyl Halides (R-X) by SN

$$R-X + H_2O \underset{\text{Reflux/Hydrolysis}}{\overset{Ag_2O}{\rightleftharpoons}} R-OH + HX$$

OR

$$R-X + KOH \underset{\text{Reflux}}{\overset{H_2O}{\rightleftharpoons}} R-OH + KX$$

← two steps are involved

Process:

(i) $R-X + H_2O \rightleftharpoons R-OH + HX$

(ii) $HX + KOH \rightleftharpoons KX + H_2O$

Mechanism of Hydrolysis

The mechanism of alkaline hydrolysis can be SN1 or SN2

$$R-X \quad \underset{3^\circ, 2^\circ, 1^\circ}{\overset{\text{SN1 increases}}{\longrightarrow}} \quad \underset{\text{SN2 increases}}{\longleftarrow}$$

For tertiary alkyl halides, mixtures are often, mixtures are often found with the major product being alkenes

$$R-\underset{\underset{R'}{|}}{\overset{\overset{R''}{|}}{C}}-X \xrightarrow[\text{reflux}]{KOH} \underset{\text{minor}}{\text{Alkanol}} + \underset{\text{major}}{\text{olefins}}$$

Here, the formation of alkenes or olefins is by elimination process i.e E1 which is competing with substitution process, SN1

$$(CH_3)_3C-Cl \xrightarrow[\text{reflux}]{KOH} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH + CH_3C(CH_3)=CH_2$$

minor (major)

③ Hydrolysis of Esters: This hydrolysis can be acid catalyzed or alkaline catalyzed

(i) $R-\underset{\underset{OR'}{|}}{\overset{\overset{O}{\|}}{C}}-H + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} RCOOH + R'OH$

(ii) $R-\underset{\underset{OR}{|}}{\overset{\overset{O}{\|}}{C}}-H + H_2O \overset{NaOH}{\rightleftharpoons} RCOONa + R'OH$

This also involves two steps

(i) $RCOOR + H_2O \rightleftharpoons RCOOH + R'OH$

(ii) $RCOOH + NaOH \rightleftharpoons RCOONa + H_2O$

$\Rightarrow RCOOR + NaOH \rightleftharpoons RCOONa + R'OH$

Example

$$\begin{array}{l} CH_2-O-\overset{\overset{O}{\|}}{C}-R \\ CH-O-\overset{\overset{O}{\|}}{C}-R' \\ CH_2-O-\overset{\overset{O}{\|}}{C}-R'' \end{array} + H_2O \overset{H^+}{\rightleftharpoons} \begin{array}{l} CH_2-OH \\ CH-OH \\ CH_2-OH \end{array} + \begin{array}{l} RCOOH \\ R'COOH \\ R''COOH \end{array}$$

Triglyceride or fat & oil

$$\begin{array}{l} CH_2-OH \\ CH-OH \\ CH_2-OH \end{array} + \begin{array}{l} RCOOK^+ \\ R'COOK^+ \\ R''COOK^+ \end{array}$$

Reduction of Carbonyl Compounds (Aldehydes and ketones): The reduction of aldehydes and ketones involves the usual reducing agents such as

(i) H_2 with catalyst eg H_2/Pt or H_2/Pd or H_2/Ni

(ii) Chemical reducing agent e.g $NaBH_4$/ether or alcohol, $LiAlH_4$/ether

(strongly reducing and)

Note that $LiAlH_4$ is a very powerful reducing agent. It reduces $-CHO$, $>C=O$, aldehyde, ketone

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$R-COOR'$ (ester) and $>C=C<$ (olefins).

However, $NaBH_4$ is a milder than $LiAlH_4$ reduces $-CHO$ (aldehyde), $>C=O$ (ketone), but no effect on $R-COOR'$ (ester) as well as $C=C$ (olefins)

2nd May, 2024

* ALDEHYDES:

On reduction

$$R-CHO \xrightarrow[\text{or } LiAlH_4/\text{ether}]{H_2/Ni} R-CH_2OH$$

1^0 alcohol

or $NaBH_4$/ether

(methanol)

e.g

$CH_3CH=CHCHO$ (but-2-ene-1-al) $\xrightarrow{LiAlH_4/\text{ether}}$ $CH_3CH_2CH_2CH_2OH$

(It is non-selective reducing agent)

$CH_3CH=CHCHO \xrightarrow[\text{or } NaBH_4/\text{methanol (MeOH)}]{NaBH_4/\text{ether}} CH_3CH=CHCH_2OH$

(Selective reducing agent)

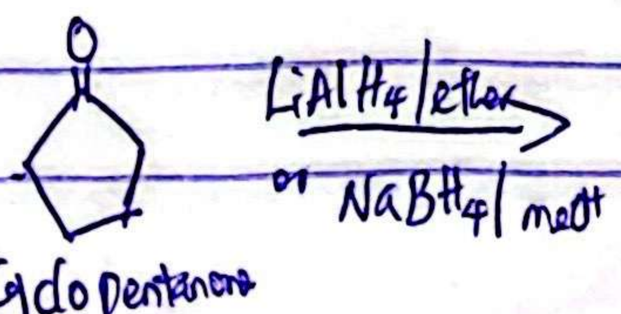
KETONES: Ketones on reduction will yield Secondary alcohols

$$R-CO-R \xrightarrow[\text{or } LiAlH_4/\text{ether}]{H_2/Ni} R-CH(OH)-R$$

2^0 alcohol

or $NaBH_4/MeOH$

eg



Esters: Esters will yield two types of alkanols will powerful reducing agents.

If ~~Sodium monohydride~~ $NaBH_4$ (a mild reducing agent is used. No reaction occurs or reduction may be very slow.

Hence, medium aluminium hydride is used

$$R-COOR' \xrightarrow[[H^+]]{LiAlH_4/\text{ether}} R-CH_2OH + R'-OH$$

Note that one of the products must be a primary alcohol, while the other depends on the basic nature of the R'

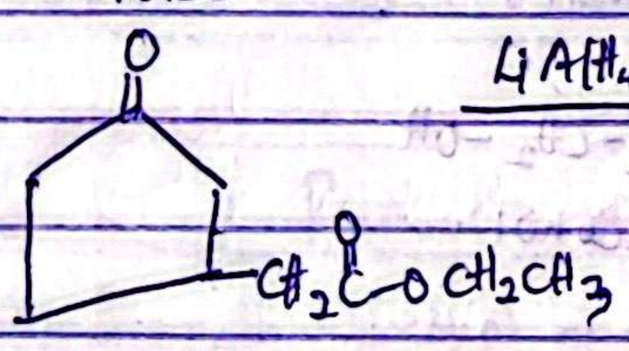
e.g

$CH_3CH_2COOCH_3 \xrightarrow[LiAlH_4/\text{Ether}]{[H]} CH_3CH_2CH_2OH + CH_3OH$

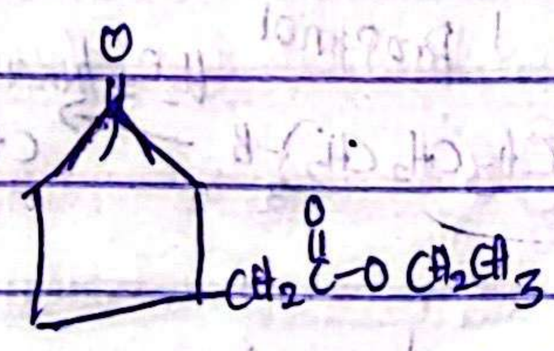
$CH_3CH_2COOCH_3 \xrightarrow[[H]]{NaBH_4/MeOH}$ No rxn

Exercise

(i)



(ii)



(6) Reduction of Carboxylic acid

The behave in a similar manner to esters. Carboxylic acids are reduced to primary alcohols (a single product) with $LiAlH_4$ (in ether while there is no reaction $NaBH_4$ in MeOH

$RCOOH \xrightarrow[LiAlH_4/ether]{[H]} RCH_2OH$ (a single product)

$\xrightarrow[NaBH_4/MeOH]{[H]}$ no rxn

e.g

$CH_3CH_2\overset{O}{\overset{\|}{C}}-OH \xrightarrow[[H]]{LiAlH_4/ether} CH_3CH_2CH_2OH$

(6)

(7) Hydroboration: This reaction is also used to convert alkene to alcohols.

It is a two step reaction process, in that the first step is conversion of alkene into trialkyle borane. Again, this is converted to alcohol in the second step

The next reaction is an anti Markovnikov addition in water across the double bond

$R-CH=CH_2 \xrightarrow[\text{THF (Tetrahydrofuran, a solvent)}]{BH_3} (R-CH_2-CH_2)_3B$ (Trialkyl borane)

$\xrightarrow{H_2O_2/NaOH} R-CH_2-CH_2-OH$ alcohol

(1) Convert 1 propene to 1 propanol

$CH_3CH=CH_2 \xrightarrow[THF]{BH_3} (CH_3CH_2CH_2)_3B \xrightarrow{H_2O_2/NaOH} CH_3CH_2CH_2OH$

1-propene

(2) Convert 2 butene to 2 butanol

$CH_3CH=\underset{CH_3}{C}H \xrightarrow[THF]{BH_3} (CH_3-CH_2-\underset{CH_3}{CH})_3B$

2-butene

$\xrightarrow{H_2O_2/NaOH}$ $CH_3CH_2\underset{CH_3}{CH}-OH$

(8) Preparation of Alcohol From Grignard Reagent: Grignard reagent is used in the synthesis of the preparation of all the three type of alcohols (1°, 2°, 3°)

The grignard reagent, ($RMgX$) are reacted with carbonyl compound (aldehydes and ketones), esters, epoxide to for intermediate which are further hydrolyzed to alkanols

(1) With aldehydes & ketones

$\overset{\delta+}{C}=O + R^{\ominus}Mg^{\oplus}X \xrightarrow[(CH_3CH_2)_2O]{\text{dry ether}}$

electrophilic site; nucleophile

$\left[R-\overset{|}{C}-O^{\ominus}-Mg^{\oplus}X\right] \rightleftharpoons R-\overset{|}{C}-OH + MgOHX$

This method has an advantage of extending the carbon chain

$RMgX + \underset{H}{\overset{H}{C}}=O \xrightarrow[(CH_3CH_2)_2O]{\text{dry ether}} H-\underset{H}{\overset{R}{C}}-O^{\ominus}Mg^{\oplus}X$

$\xrightarrow{H^+/H_2O} R-\underset{H}{\overset{H}{C}}-OH + MgOH$

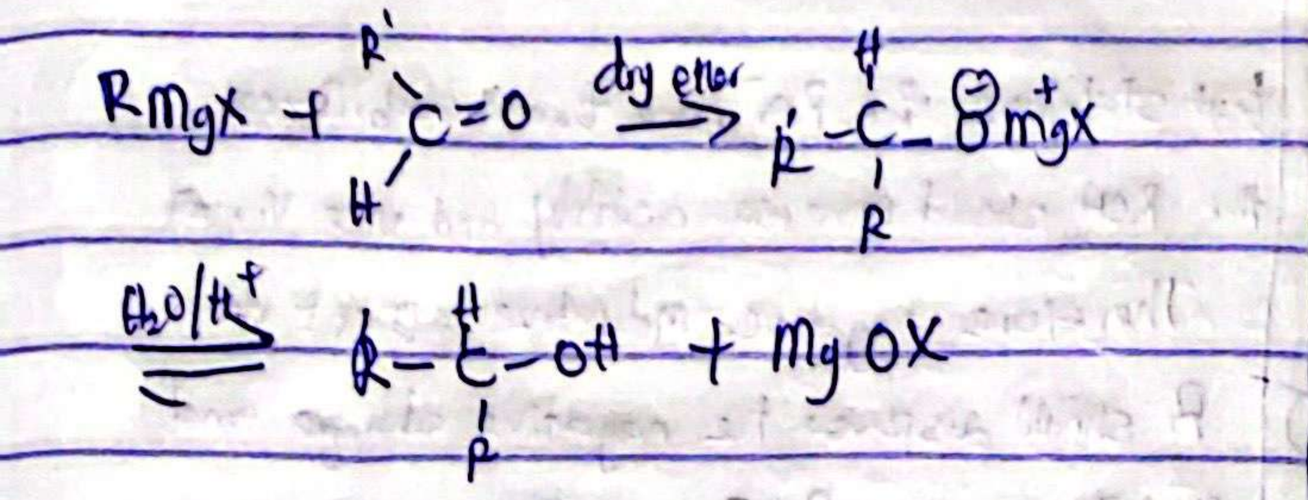
1° alcohol (+1 C-atom)

Epoxy ethane (ethylene oxide) may be used instead of methanol

$RMgX + H_2C\text{—}CH_2$ (epoxy ethane) $\xrightarrow{\text{dry ether}} RCH_2CH_2O^{\ominus}Mg^{\oplus}X$

$\xrightarrow{H_2O/H^+} RCH_2CH_2OH + MgOHX$

1° alcohol (+2 C atoms)

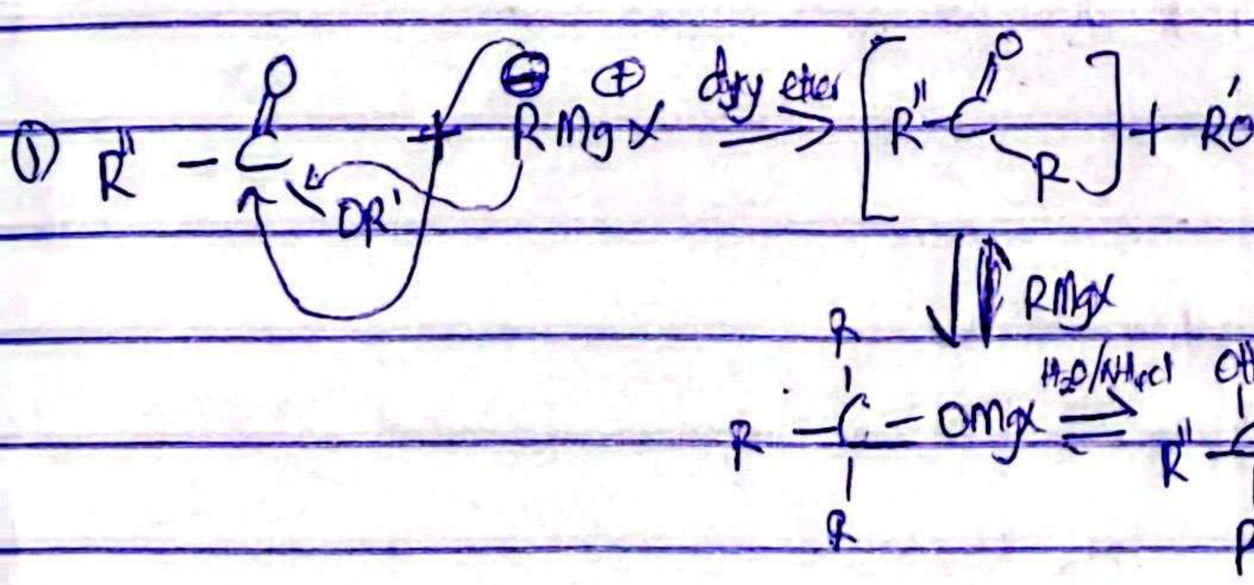


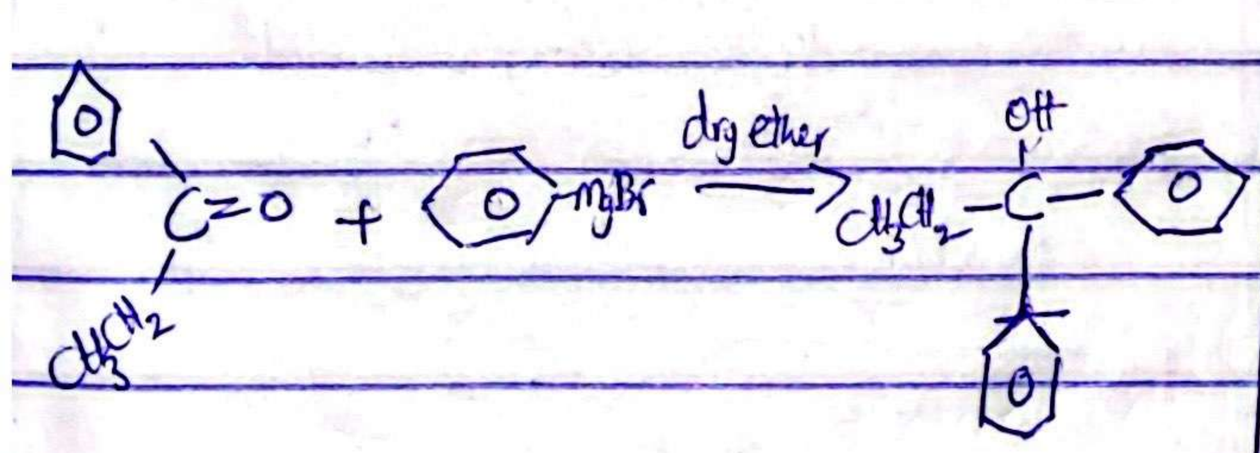
3rd May, 2024

In the preparation of tertiary alcohol, aqueous NH4Cl is used for hydrolysis as dilute acid brings about dehydration (i.e H_2O + H^+) of the alcohol to alkene

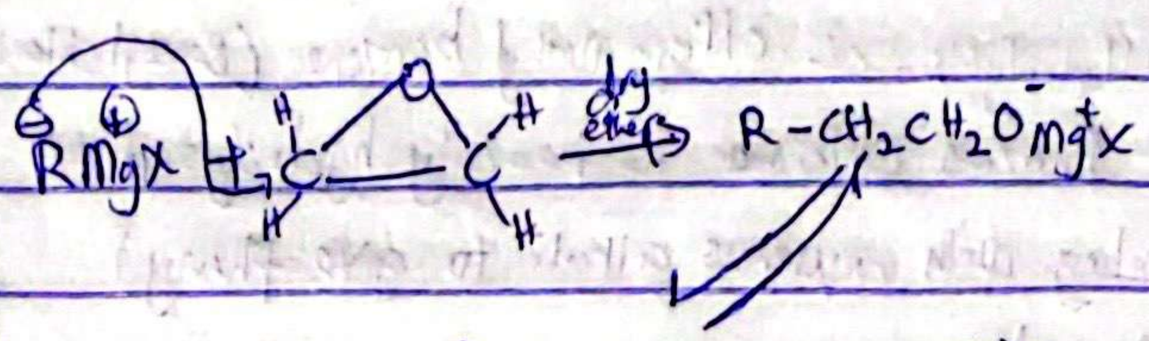
② With Esters

The reaction of grignard reagent and esters gives tertiary alcohol as the product. It is a two step reaction. The first step, gives ketone.





③ With Epoxide: The reaction of grignard reagent and epoxide gives a primary alkanol with two carbon atoms added



How do you prepare propanol from a named grignard reagent

In Summary:

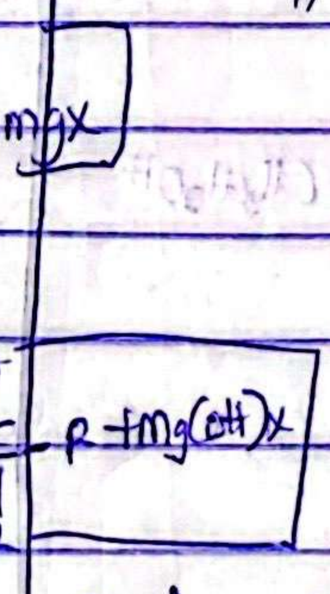
Grignard Reagent + Methanol → 1° alcohol

" + other aldehyde → 2° alcohol

" + ketone → 3° alcohol

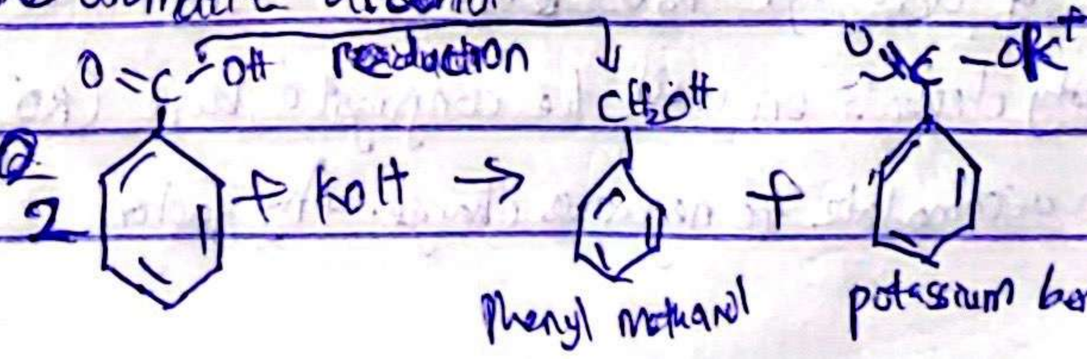
" + esters → ketone → 3° alcohol

" epoxide → 1° alcohol



Preparation of Aromatic Alcohol

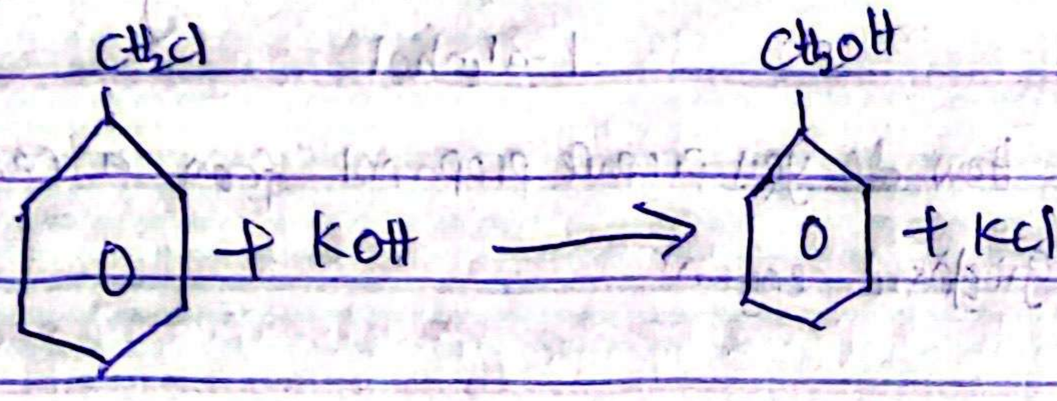
(1) Aromatic alcohol can be prepared by Cannizaro an. Aromatic aldehyde, such as benzaldehyde, when shaken with aqueous KOH, it undergoes simultaneous oxidation and reduction (disproportionation reaction) yielding the potassium salt of the corresponding carboxylic acid together with the aromatic alcohol



The potassium salt is dissolved in water and the alcohol is extracted with ethoxyl ethane (diethyl ether) using seperating funnel.

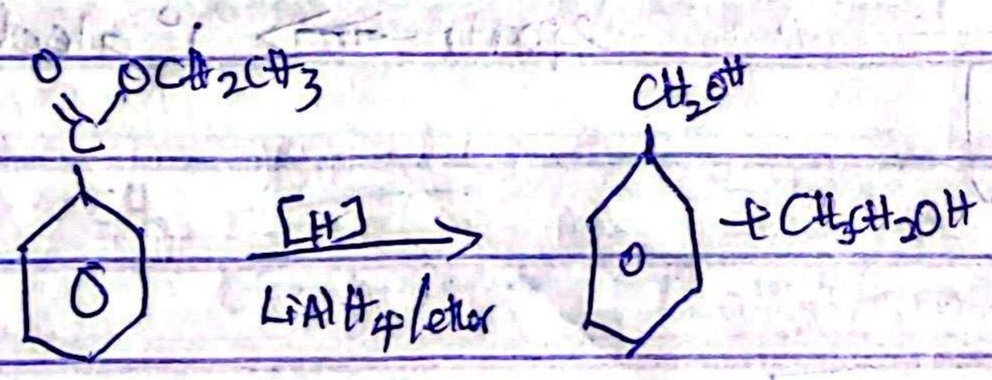
② Hydrolysis of chloromethyl benzene (Benzyl chloride)

Benzide chloride is readily hydrolysed on boiling with aqueous alkali to give phenyl ethanol



③ By reduction of Benzene Carboxylate (Benzoate)

Benzylcarboxylic acid (benzoic acid) or ether benzoate can be reduced to the alcohol by using $LiAlH_4$ (reducing agent)



Chemical Reactivies of Alkanol

(I) Alkanols have Amphoteric behaviour. Alkanols can act as an acid and a base

(i) As an acid: An alcohol releases a proton

$$R-O-H \rightleftharpoons RO^- + H^+$$

acid — conjugate base alkoxy

Order of acidity: $H_2O > CH_3OH > 1^\circ$ alcohol $> 2^\circ$ alcohol $> 3^\circ$ alcohol

Acidity depends on well the conjugate base (RO^-) can accomodate the negative charge. Any factor that stabilizes the RO^- more than it stabilizes the ROH should increase acidity and vice versa

Therefore negative inductive effect in R should disperse the negative charge and stabilizes the RO⁻ and thus increases acidity. On the other hand, positive inductive effect in R should intensify the negative charge on (RO^-), Next stabilizes the anions (RO^-) and thus decreases acidity

The acidity of alkanols is shown by their reaction with active metals to liberate H_2 gas and give the metal alkoxides

$$2Na + 2H_2O \rightarrow 2NaOH_{(aq)} + H_2$$

$$2Na + 2R-OH \Rightarrow 2RO^-Na^+ + H_2$$

Example

$$R-O-H + 2M \rightarrow 2RO^{\oplus}M^{\oplus} + H_{2(g)}$$

(M = metal)

Where M is metal

$$2CH_3CH_2OH + 2Na \rightarrow 2CH_3CH_2O^{\ominus}Na^{\oplus} + H_2O$$

(ii) As a base. Alkanol accepts a proton using a lone pair of electron on oxygen atom.

$$R-OH + H^{\oplus} \rightarrow ROH_2^+ \rightarrow \text{oxonium}$$

The basicity of alkanol is shown by the reactions of hydrogen halides to give alkyl halides (RX)

$$ROH + HX \rightarrow RX + H_2O$$

(base: ROH; acid: HX)

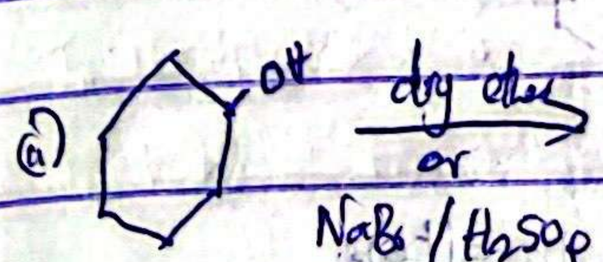
HI reacts most rapidly; while HCl least rapidly and requires the presence of Zinc chloride for reaction with

* oily
* homogeneous
* layer

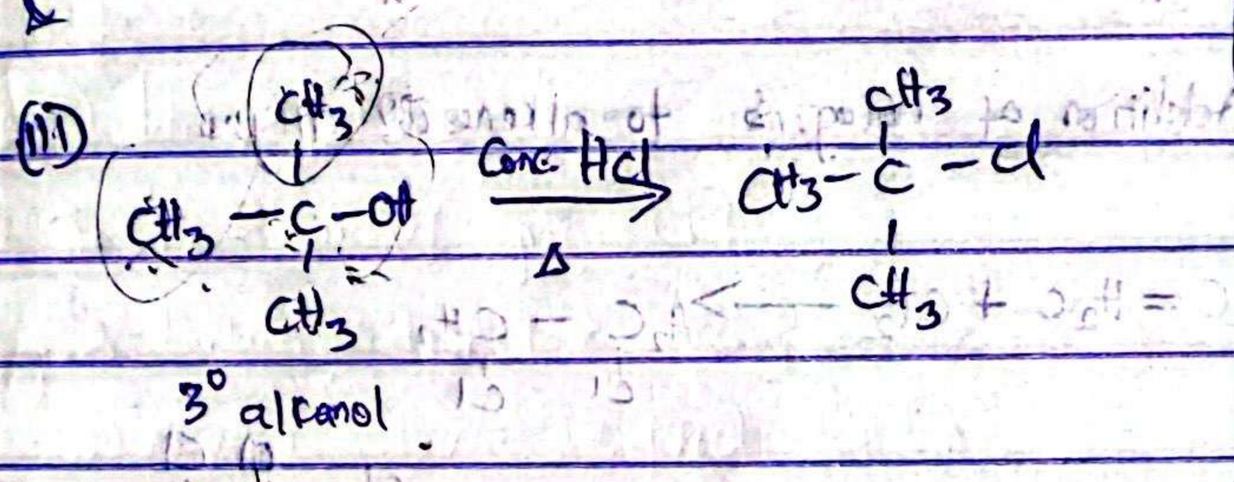
primary and secondary alkanol.

But conc HCl at room temperature is right for tertiary alkanols. This test is called Lucas test for alkanols

(i) $CH_3CH_2CH_2OH + HCl \xrightarrow[\Delta]{ZnCl_2} CH_3CH_2CH_2Cl$

(ii) 

$(2NaBr + H_2SO_4 \rightarrow 2HBr + Na_2SO_4)$

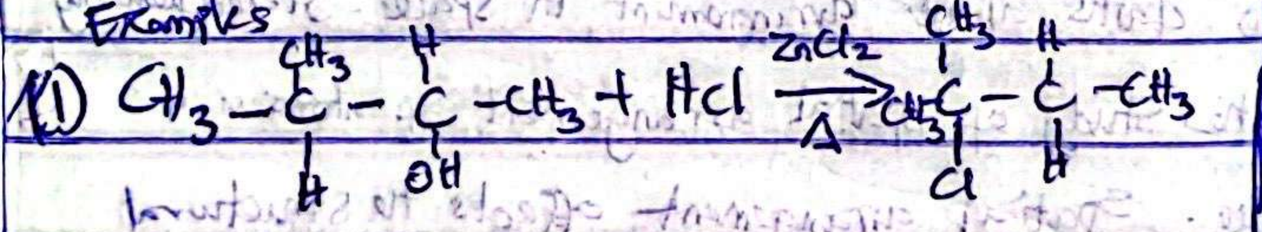
(iii) 

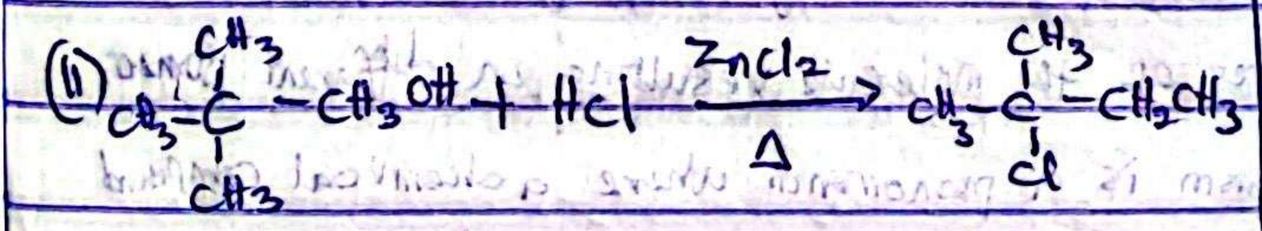
3° alkanol

Note: (i) The reaction is catalyzed by acid. eg Conc. H_2SO_4

(ii) Rearrangement of alkyl group may occur except with some primary alkanol

Examples

(i) 

(ii) 

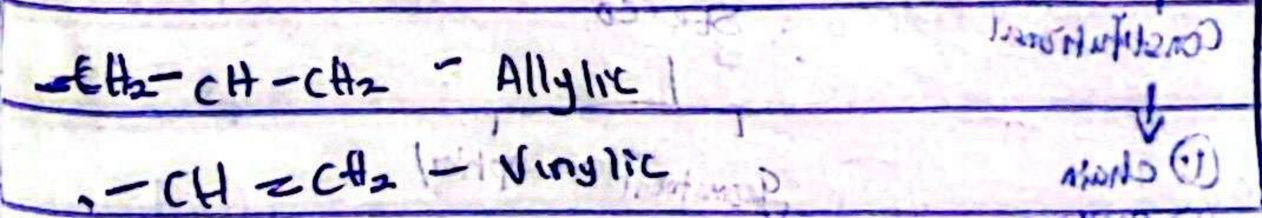
Order of Reactivity of Alkanol toward Hydrogen Halides

Benzyl, Allyl > 3° > 2° > 1° > CH_3OH

SN1 | SN2

$CH_2 = CH - CH_2$ - Allylic

$-CH = CH_2$ - Vinylic



Mechanism of Reaction

The mechanism of the reaction between an alkanol and HX is SN1 except for methanol and most primary alkanol where SN2 is preferred.

The SN1 mechanism involves 3 major steps;

(i) Protonation of Alkanol to for oxonium ion (H_3O^+)

(ii) Dissociation of the protonated Alkanol into water and a carboncation

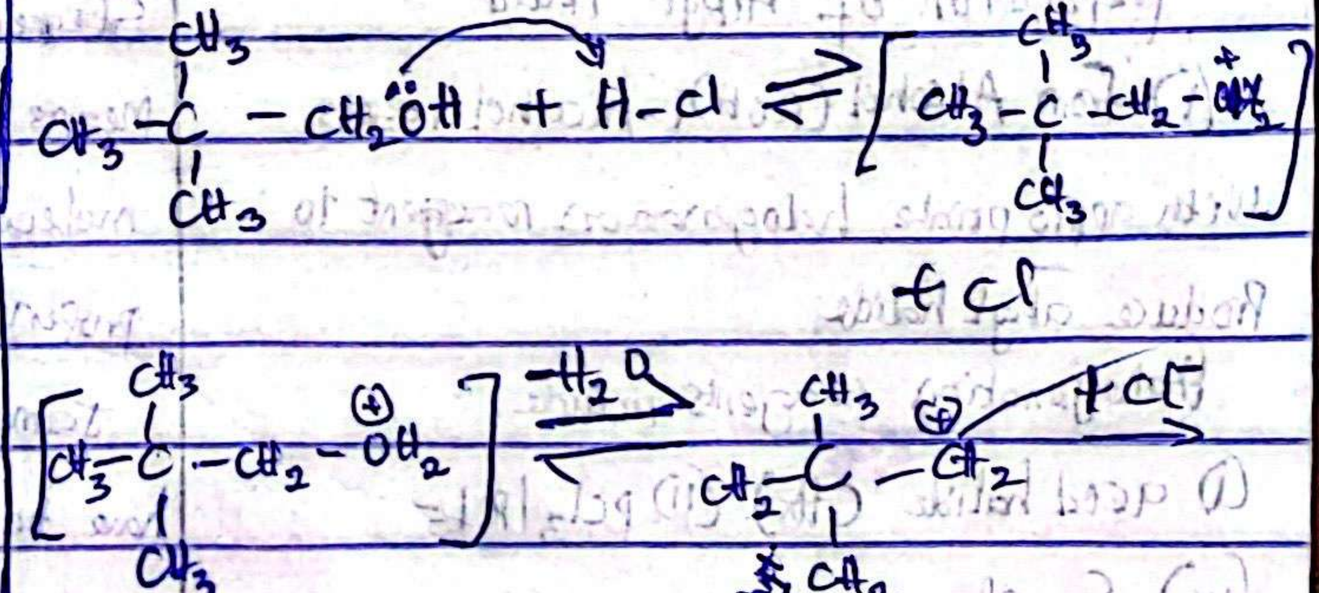
(iii) Combination of the carbocation or rearranged carbocation with halide ion (X^-) to form the alkyl halide

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

(ii) $R-\overset{(+)}{O}H_2 \underset{\text{slow}}{\rightleftharpoons} R^+ + H_2O$

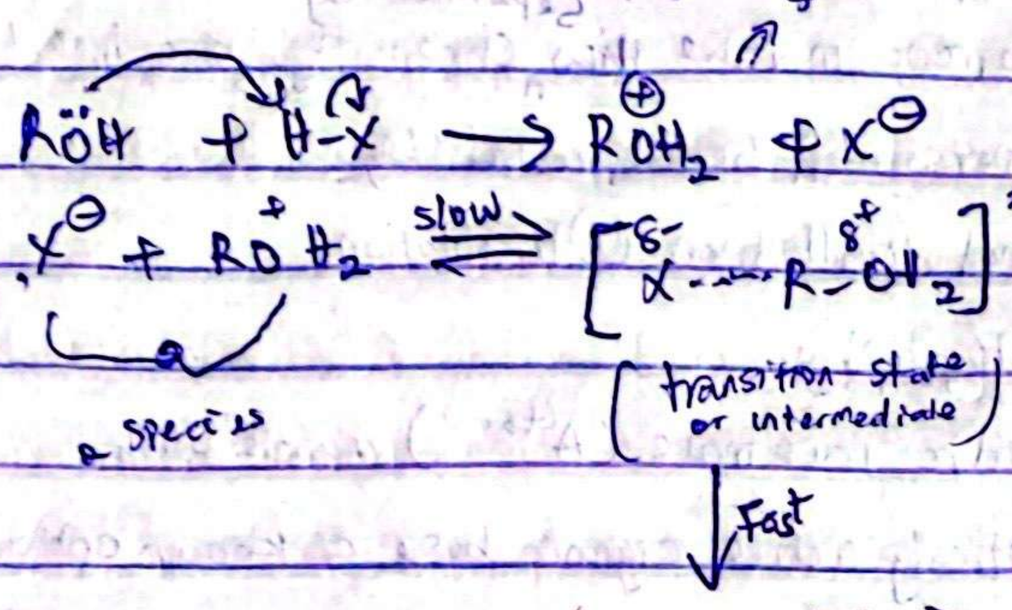
(iii) $R^+ + X^- \xrightarrow{\text{fast}} RX$

The slow one is the rate determing step consisting of only one molecule i.e $R-\overset{+}{O}H_2$, therefore it is SN1 (Unimolecular)



For most primary alkanol and methanol the formation of primary carbocation is very slow because of the poor accomodation of positive charge. Hence, bimolecular attack is unhindered

i.e SN2 is fast



$\therefore X-R + H_2O$

2 species in the slow step showing that the mechanism is bimolecular.

7th May, 2020

Alkanol can also be converted to alkyl halides by reaction with thionyl chloride ($SOCl_2$) or Phosphorus pentachloride (PCl_5) or PCl_3

$ROH + SOCl_2 \longrightarrow RCl + HCl_{(g)} + SO_{2(g)}$

$ROH + PCl_5 \longrightarrow RCl + HCl_{(g)} + POCl_3$

steamy white fume

$3ROH + PX_3 \longrightarrow R-X + P(OH)_3$

X = any of halides except fluorine

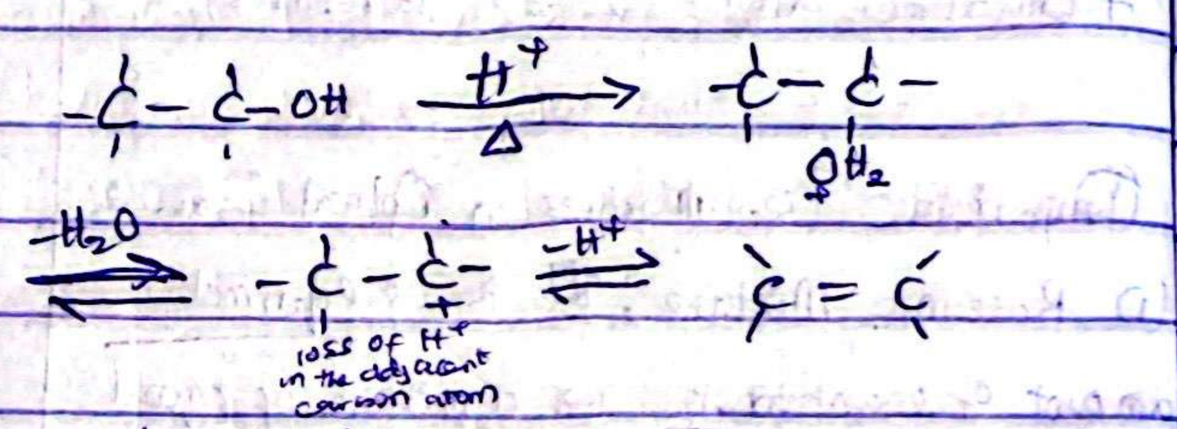
The advantage of the ~~first~~ third reaction over others is that it does not contain contaminant as gases.

The steamy white fumes with PCl_5 ~~Contains~~ indicates presence of OH group in a compound, especially alkanols and alkanonic acid

$RC(=O)OH + PCl_5 \longrightarrow RC(=O)Cl$

② Dehydration of Alkanols: ~~It~~ It gives alkenes, if there is a total dehydration or alkoxyalkanes if there is partial dehydration

The common reagent for dehydration is conc. H_2SO_4 or H_3PO_4 (orthophosphoric acid or phosphoric acid). Also, alumina (Al_2O_3), with heat



* Order of dehydration

$3^\circ > 2^\circ > 1^\circ > CH_3OH$

The reaction in the absence of a nucleophile (excess conc. H_2SO_4) gives olefin. The intermediate carbocation may rearrange to a more stable one in form of 1, 2 hydride shift or 1, 2, alkyl shift before losing a proton in the adjacent carbon atom to form olefin

The above carbocation is susceptible to attack by nucleophile, hence if excess alkanol is used, the alkanol may act as the nucleophile because of the excess lone pair of lone pair of electron on the oxygen atom

General Reaction

$R-OH + H^+ \longrightarrow R\overset{\oplus}{O}H_2 \xrightarrow{-H_2O} R^{\oplus} \xrightarrow[\text{No excess alkanol}]{-H^+}$ Alkene

$\downarrow$ with excess alkanol (ROH)

$R-O-R$ (ether)

Depending on the condition of dehydration, alkanols may give two types of product

(i) $ROH \xrightarrow[180^oC]{\text{excess conc. } H_2SO_4}$ Alkene

(ii) $ROH \xrightarrow[145^oC]{\text{Conc. } H_2SO_4}$ Alkoxyalkane (ether)

Examples

$(CH_3)_3C-CH_2OH \overset{H^+}{\rightleftharpoons} (CH_3)_3C-CH_2OH_2 \rightleftharpoons (CH_3)_3C-\overset{\oplus}{C}H_2 + H_2O$

$(CH_3)_3C-\overset{\oplus}{C}H_2 \xrightleftharpoons{1,2\text{-alkyl shift}} CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2CH_3$

No. excess alkanol, $-H^+$ from adjacent C-atom

$CH_2=\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2CH_3$ + $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}=CHCH_3$

minor — major product

excess alkanol, $-H^+$

$(CH_3)_3C-CH_2\overset{\oplus}{O}H_2$ (with $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2CH_3$)

$\downarrow$

$CH_2-O-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2CH_3$

(3) Formation of Esters (Esterification)

Alcohols and carboxylic acid reacts in the presence of mineral acid e.g Conc. H_2SO_4 as a catalyst to give esters

(i) $R'-OH + R-\overset{O}{\overset{\|}{C}}-OH \underset{\text{reflux}}{\overset{H^+}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-OR + H_2O$

Alcohol can also react with acid chloride

(ii) $R-\overset{O}{\overset{\|}{C}}-Cl + R'OH \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-OR + HCl$

acid chloride

(iii) $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + R'OH \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-OR + RCOOH$

acid anhydride

8th May 2024

(2) Oxidation

Alcohols can be oxidized by various oxidizing agent; (i) Aldehyde (ii) Ketone (iii) Carboxylic acid, depending on the nature of the alcohol and the strength of the oxidizing agent used

(i) $R-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow{-[H]} R-\overset{O}{\overset{\|}{C}}-H$

PCC — mild oxidizing agent

$\xrightarrow[\text{[O]}]{K_2Cr_2O_7/H_2SO_4}$ — strong oxidizing agent

$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[H^+]{K_2Cr_2O_7} R-\overset{O}{\overset{\|}{C}}-OH$

Secondary alcohol are oxidized to ketone under normal condition

$R-\overset{H}{\underset{R}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow[-[2H]]{K_2Cr_2O_7/H^+} R-\overset{O}{\overset{\|}{C}}-R$

Ketone

$CH_3-\overset{CH_3}{\underset{H}{\overset{|}{\underset{|}{C}}}}-OH \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}=O \xrightarrow{[O]} CH_3-\overset{O}{\overset{\|}{C}}-OH + CO_2$

2-hydroxyl propane

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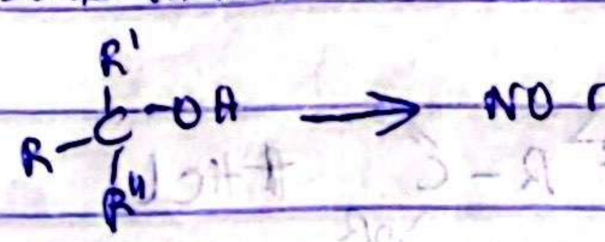
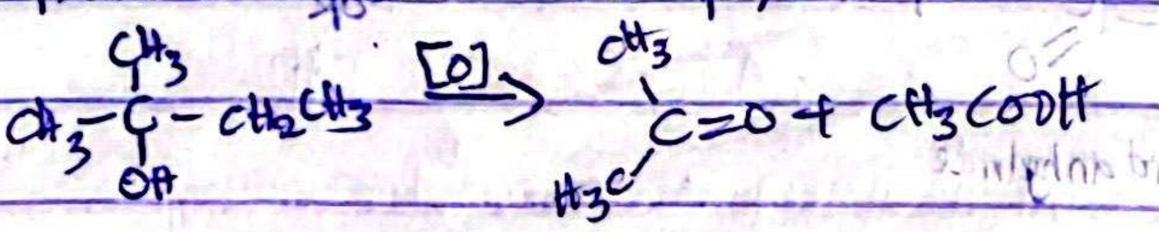
The before formed has to undergo prolonged and drastic treatment because it can be broken down into acids with smaller number of carbon atoms

Tertiary alcohols are normally resistant to oxidation, in both neutral and alkaline medium because it will involve the breakage of the high energy C-C bonds in the alcohol



3° alcohol

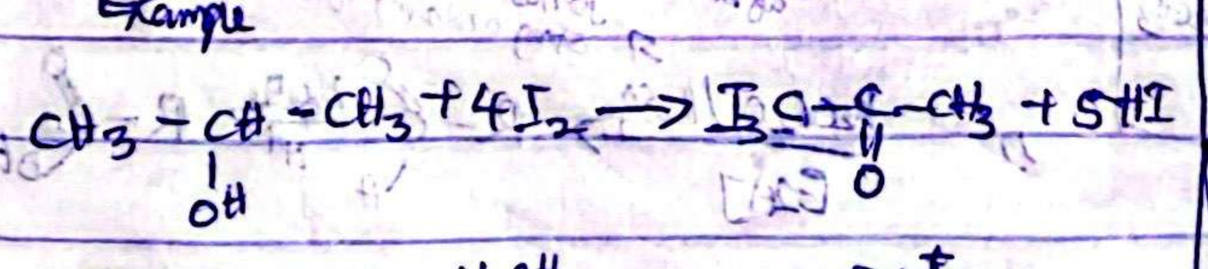
However, in acidic solutions, tertiary alcohol can be oxidized to give a mixture of ketone and acids, both with fewer carbon atom. For example;

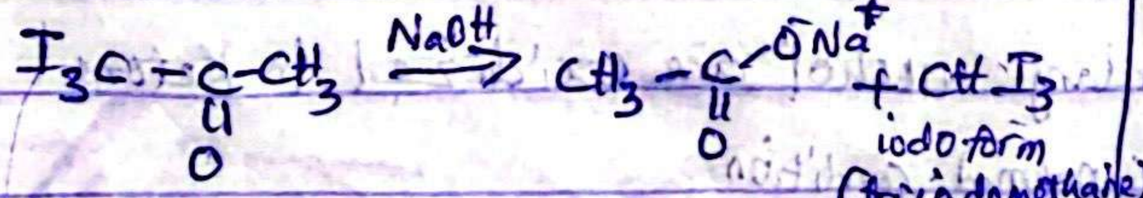


⑤ Haloform Reaction: Alcohols which contain the group $CH_3CH(OH)-$ can be oxidized under suitable conditions to $CH_3-C(=O)-$. This group of alcohol will readily undergo haloform reaction

Note that Flourine cannot be a reagent in haloform reaction

Example





CHI_3 is a yellow ppt with antiseptic smell

The haloform reaction take place in step

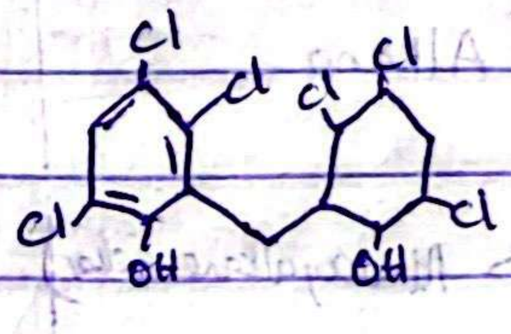
Steps:

(1) oxidation of the alcohol to an aldehyde or ketone
(2) Substitution of the halogen atom on the methyl group
(3) Hydrolysis under alkaline condition to form the haloform.

Phenol

Phenols are hydroxyl compounds all with general formular $Ar-OH$, where Ar is aryl or phenyl group. Phenols, differs from alkanols in having the -OH group directly attached to an aromatic ring. Like alcohols, they may be mono hydric or polyhydric, depending on the number of OH group that they contain.

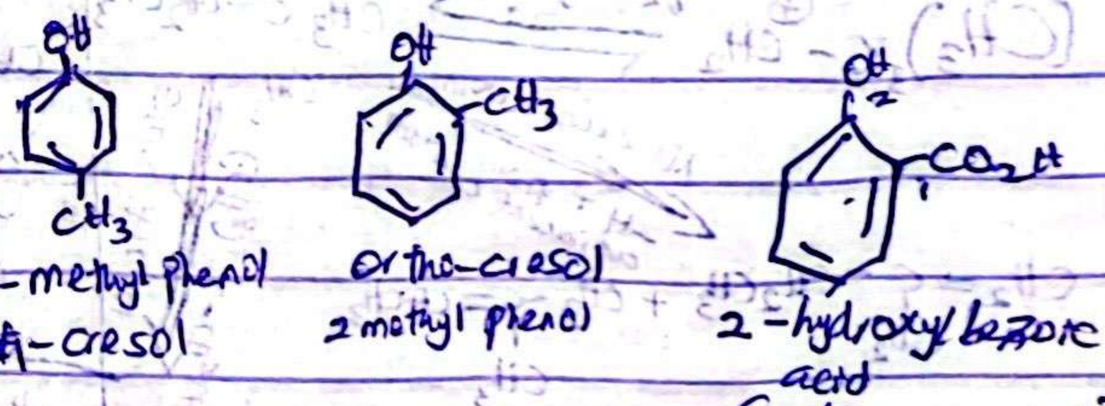
The chemistry of phenol is very different from that of alcohols. A phenolic compound hexachlorophene is consituent of mouth washes, deodorant soap and medicinal skin cleanser

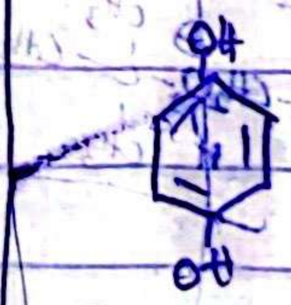


→ Acts on anti bacteria activities (ii)

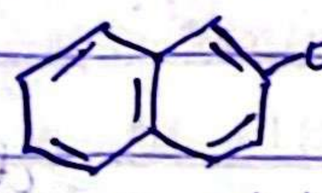
Phenols are generally named as derivatives of the simplest member of the family, Phenol

occasionally, phenols are named as hydroxyl compounds. The methyl phenols are known as CRESOLS





benzene-1,4-diol



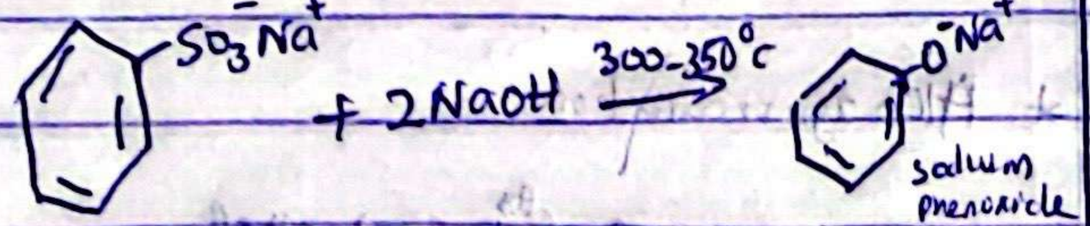
2 → naphthol
β - naphthol

Class

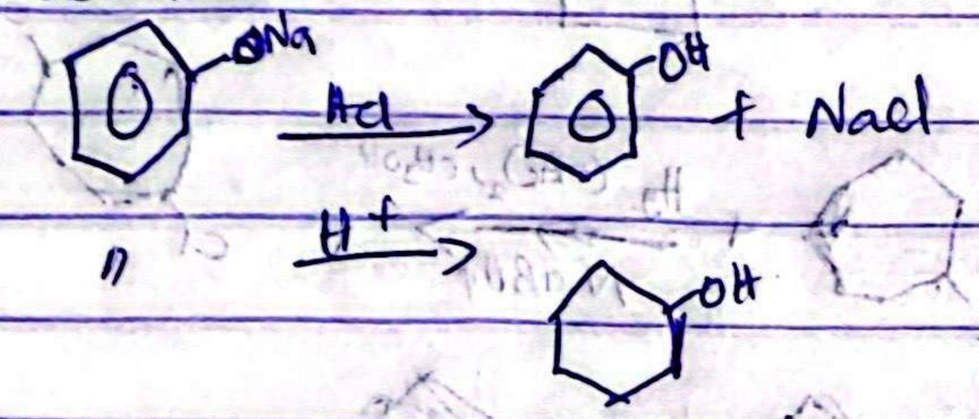
10th May, 2024

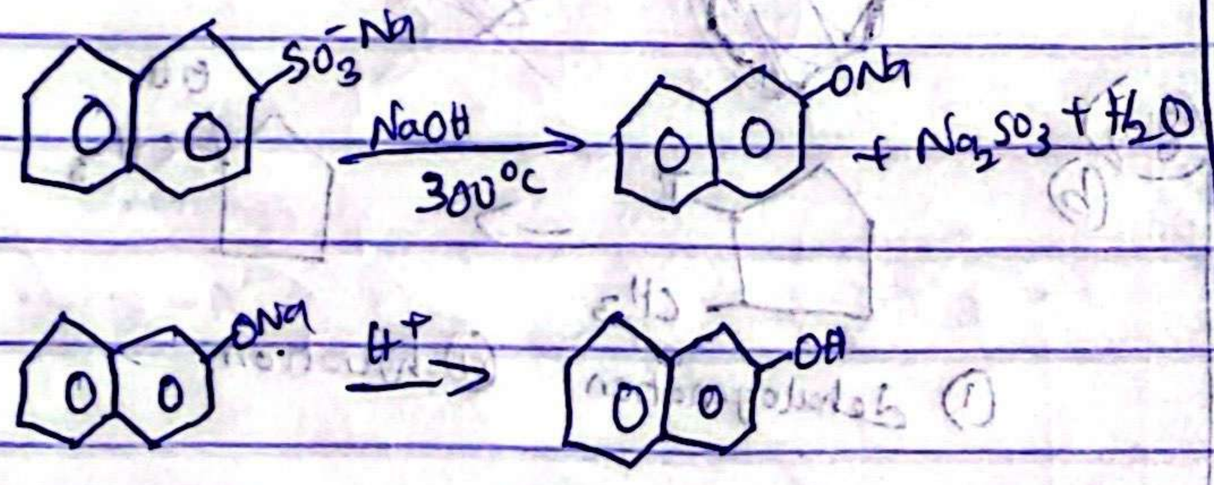
Preparation of Phenol

(1) By Diffusion of Aromatic Sulphonic salt with an alkaline solution e.g NaOH



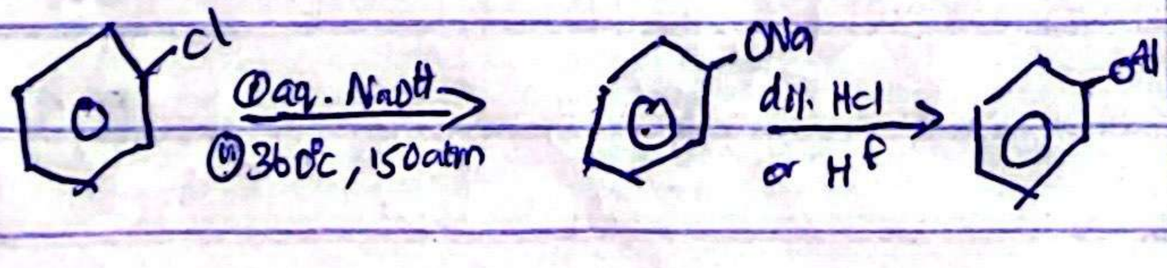
The phenol is obtained as an oily liquid by dissolving sodium phenoxide in water and acidified.



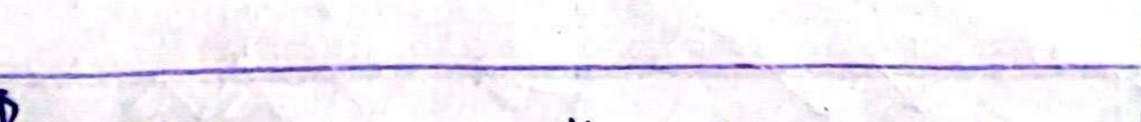


B-nephthol

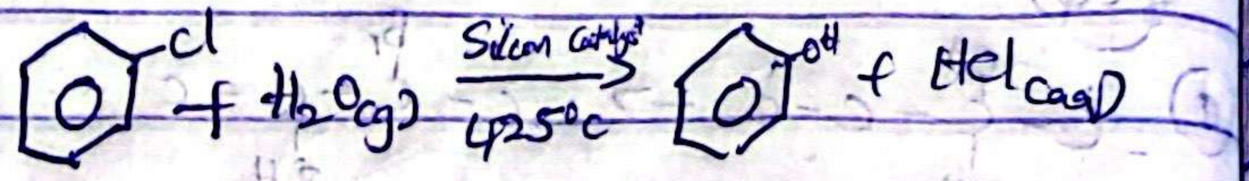
(2) By hydrolysis of chlorobenzene: Hydrolysis of Chlorobenzene by aqueous NaOH at 360°C and 150 atm



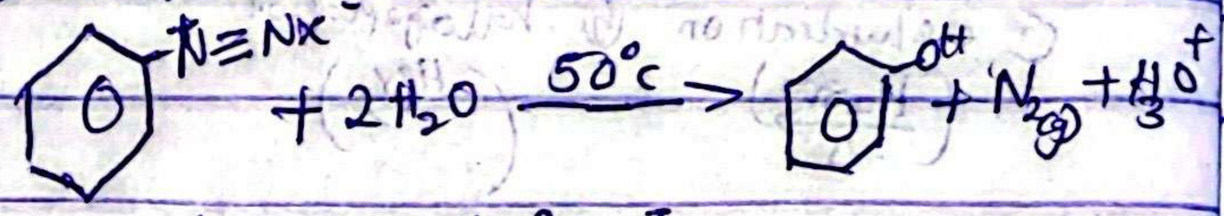
(3) By Rasching process: Here, benzene is chlorinated by passing the vapour together with HCl gas and air over a heated $CuCl_2$ catalyst at 230°C



The chlorobenzene formed is then catalytically hydrolysed by passing it with steam over silicon catalyst at 425°C



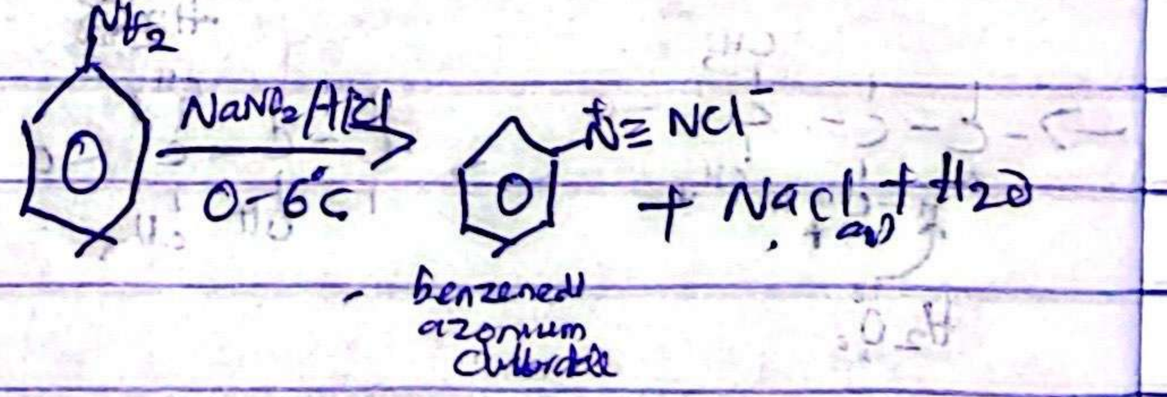
(4) By hydrolysis of diazonium salts: In the Lab, heating of solution of benzene diazonium salt on a water bath at 50°C yields phenol



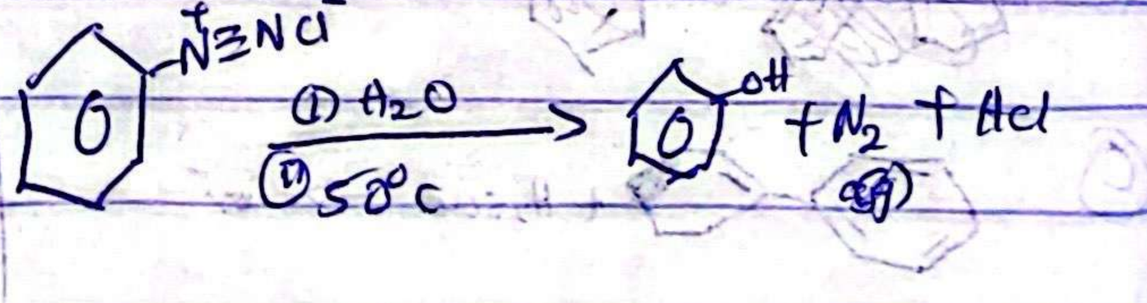
where X = Cl, Br, I.

The phenol is recovered by steam distillation and extracted with ether (diethyl ether) using a seperating funnel

Primary aromatic amine with cold nitrous acid in the presence of strong mineral acids to give diazonium salt. The process is known as diazotization



Reaction of diazonium salt with water will now give us phenol



Reactions of phenol

The reactions of phenol includes the following:

(i) Acidity of Phenol
(ii) Ether formation (Williamson Synthesis)
(iii) Ester formation
(iv) Ring substitution reaction e.g Nitration, Sulphonation, halogenation, friedal craft acylation, coupling with diazonium salt, carbonation, formylation.

Acidity of Phenol

Phenols are tremendiously more acidic than alkanol but carboxylic acid.

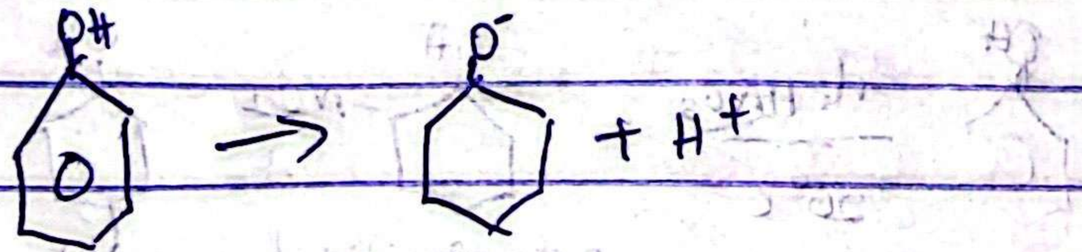
Order of acidity:

RCOOH > Phenol > alkanols

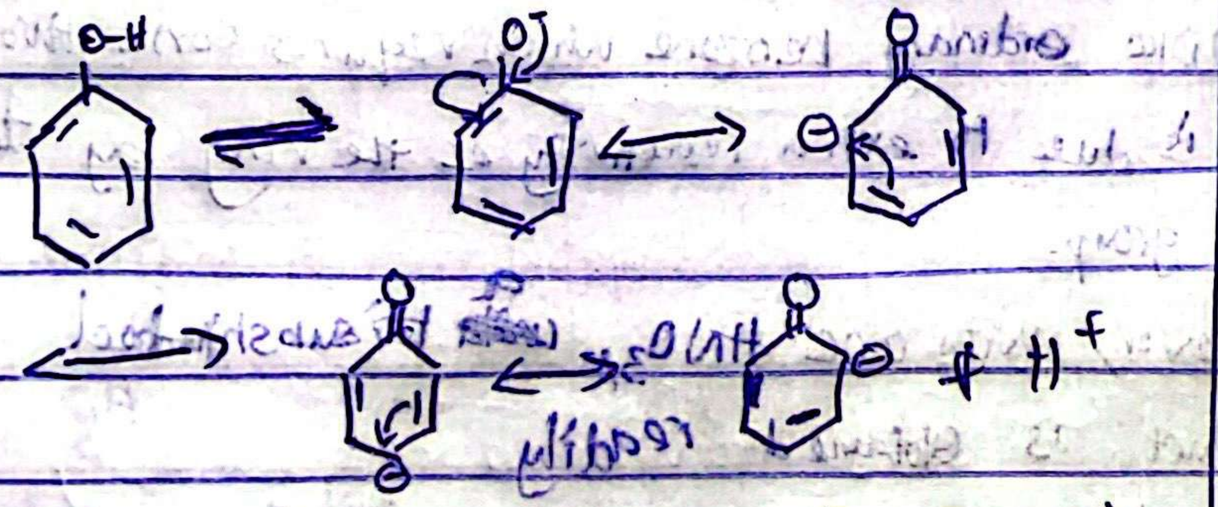
This shows that the OH group attached to an aromatic ring is so more acidic than that attacked to an alkyl group

13th May, 2020

Phenol as an acid:



The reason why phenol is more acidic is because of stabilization of phenoxide ion

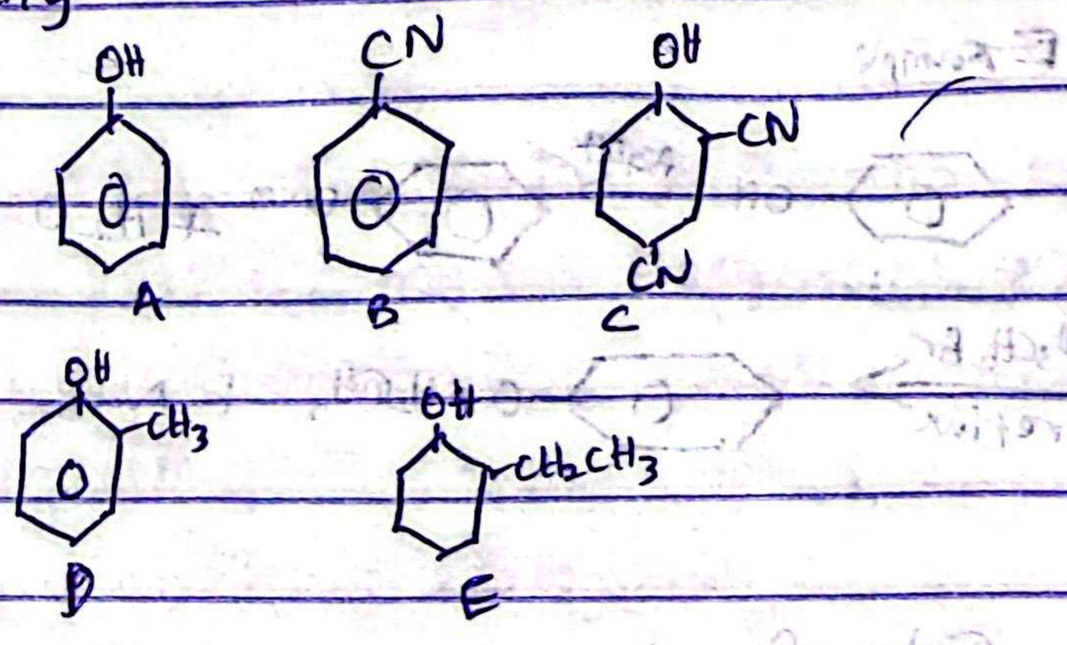


If compared with alcohol, $ROH \rightleftharpoons RO^- + H^+$ (not stabilized)

In the resonance stabilization of phenoxide ions, position 2, 4, and 6 i.e ortho and para position are more activated than other position, therefore electrophilic attack of the benzene ring will occur at ortho and para position.

Electron withdrawing group such as CN^-, Cl^-, NO_2, attacked the ortho and para position stabilized the phenoxide and thus increase acidity.

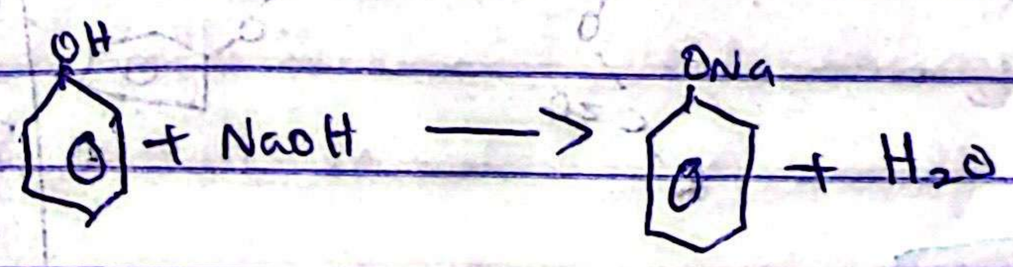
On the hand, electron donating group (R) attached to ortho and para position of phenol destabilizes the phenoxide ion and therefore decreases acity



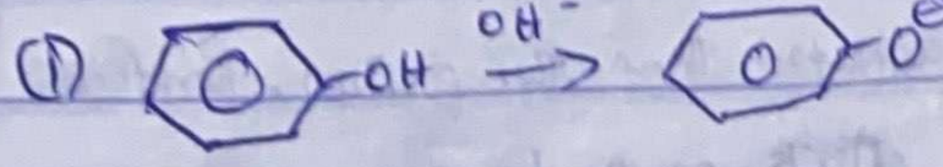
order of acidity

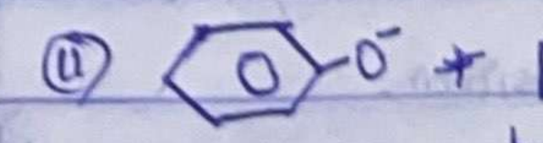
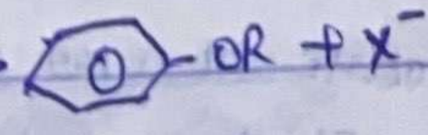
E < D < A < B < C

The acidity of Phenol is demostrated by its ability to form salts with alkaline bases such as NaOH / KOH



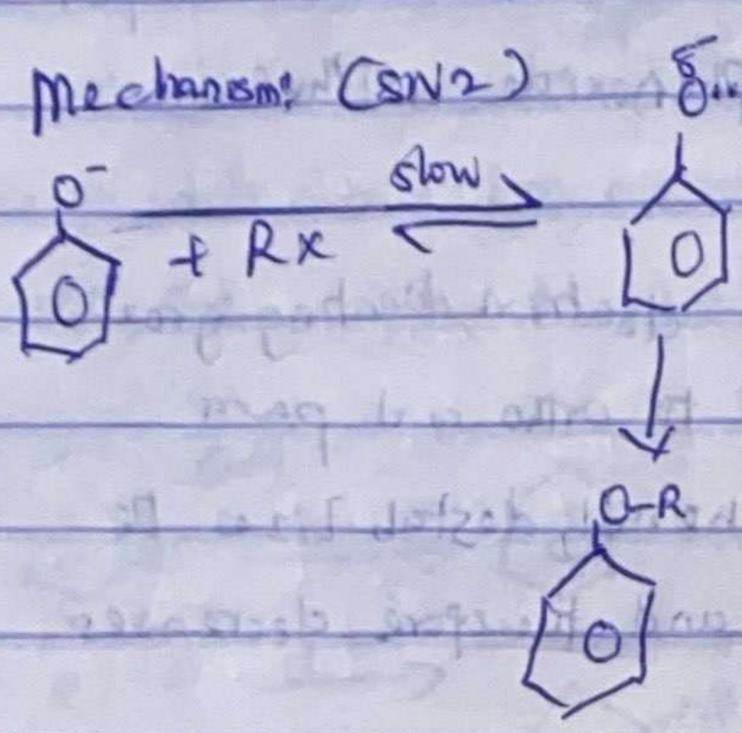
(2) Williamson's Synthesis (formation of ethers); Phenols in the presence of alkaline base (NaOH/KOH) reacts with haloalkane to form alkoxyethane/ether

(i)  $\xrightarrow{OH^-}$

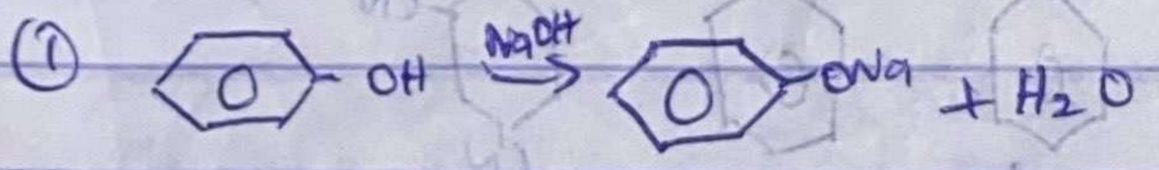
(ii)  + R–X (haloalkane) →  + X^-

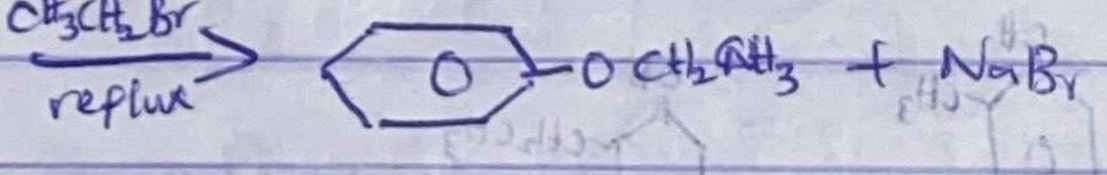
This is an SN2 reaction

Mechanism (SN2)



Example

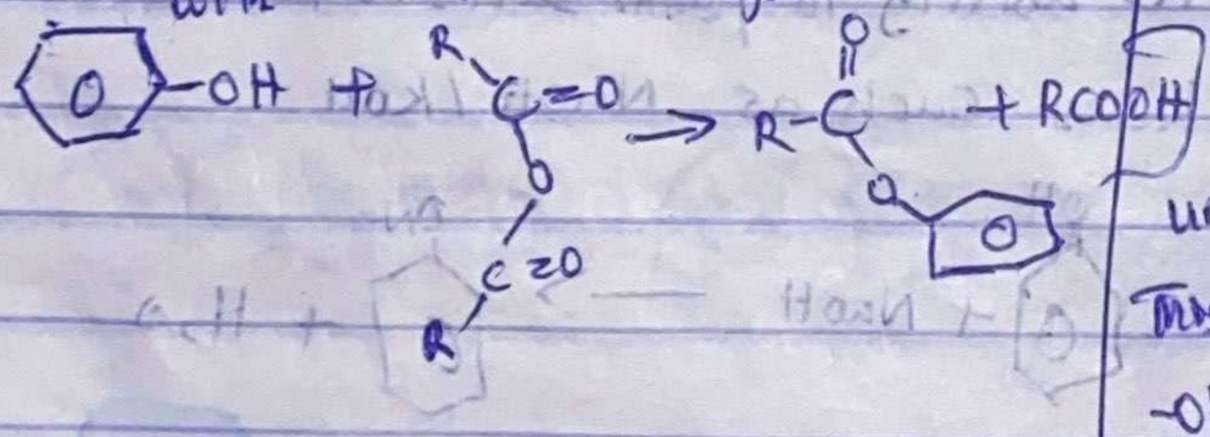
(1) 



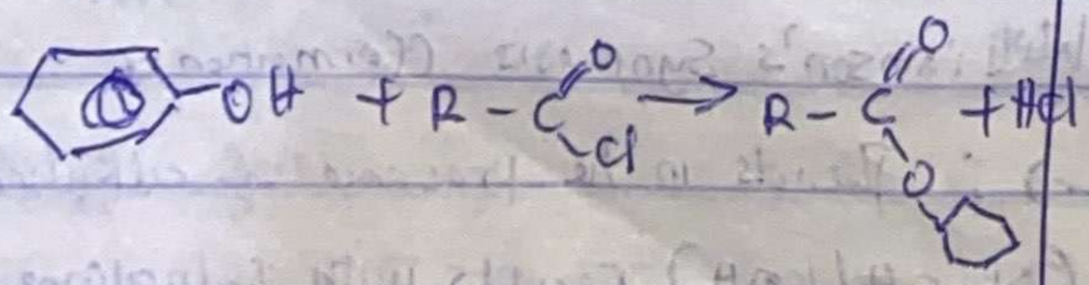
(5) Ester formation

Phenols reacts with carboxylic acid anhydride ($(RCO)_2O$), acetyl chloride $R-\overset{O}{\overset{\|}{C}}-Cl$ to form esters

with carboxylic acid anhydride



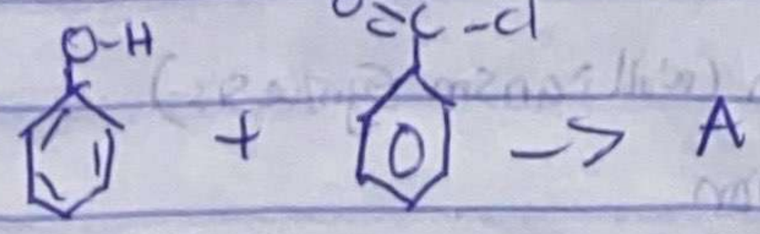
with acetyl chloride

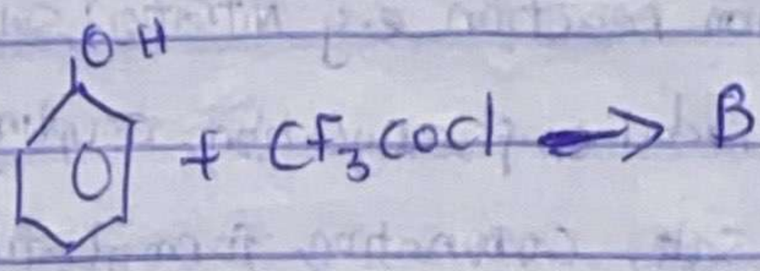


The second reaction is preferable because it does not need seperation of products

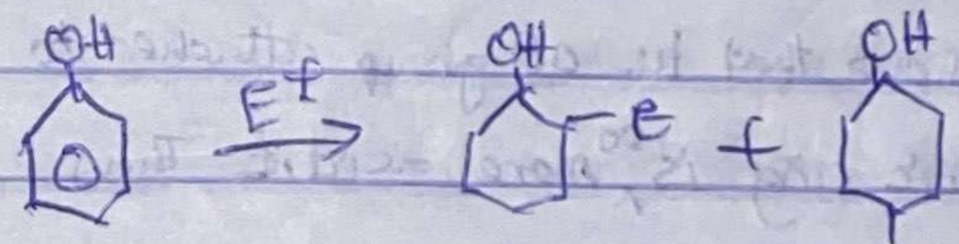
Ortho & para position are active as Phenol

as HCl has been eliminated as a gas.

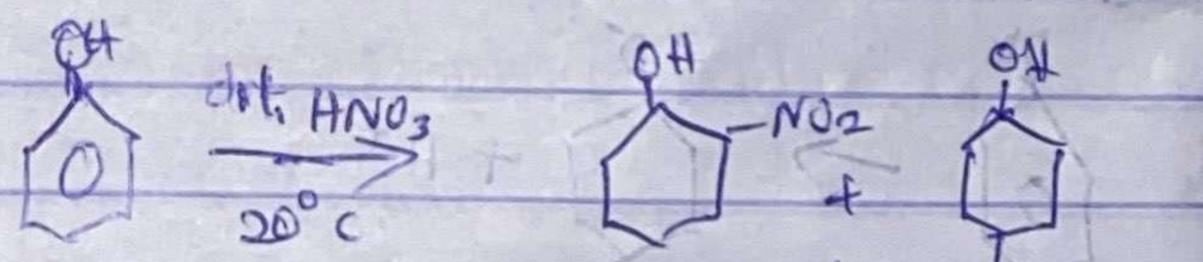
(1) 

(2) 

(4) Ring Substitution : The OH group attached to the benzene ring in phenol activate the ring powerfully and direct ortho and para in electrophilic aromatic substitution

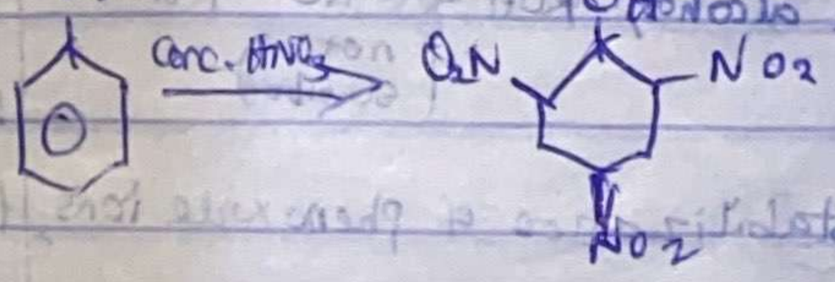


(1) Nitration : Monosubstituted Compound is obtained with dilute HNO_3 at room temperature



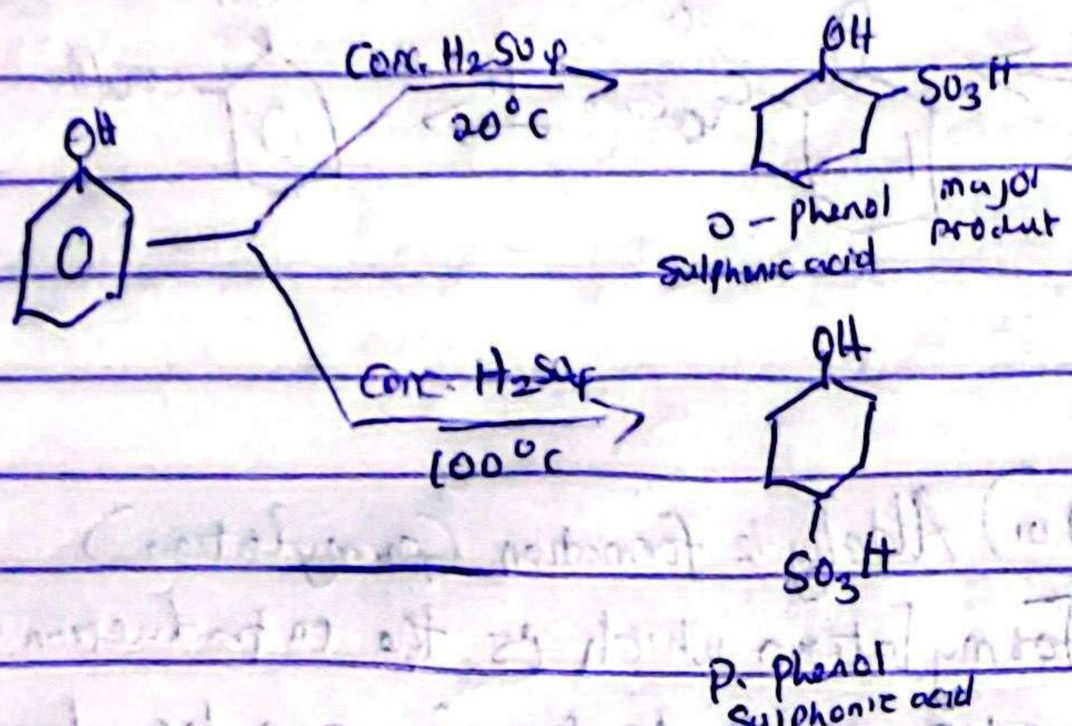
Dilute HNO_3 at 20°C will activate the reaction unlike ordinary benzene which requires conc. HNO_3. This is due to extra reactivity of the ring by the -OH group.

However, with conc HNO_3 disubstituted product is obtained readily



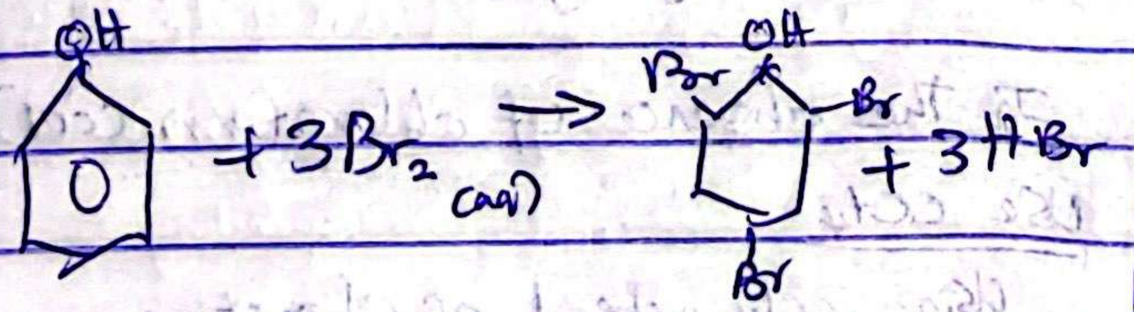
2, 4, 6 trinitrophenol

(ii) Sulphonation: When phenol is treated with conc. H_2SO_4. Different substituted product will be obtained depending on the reaction temperature.

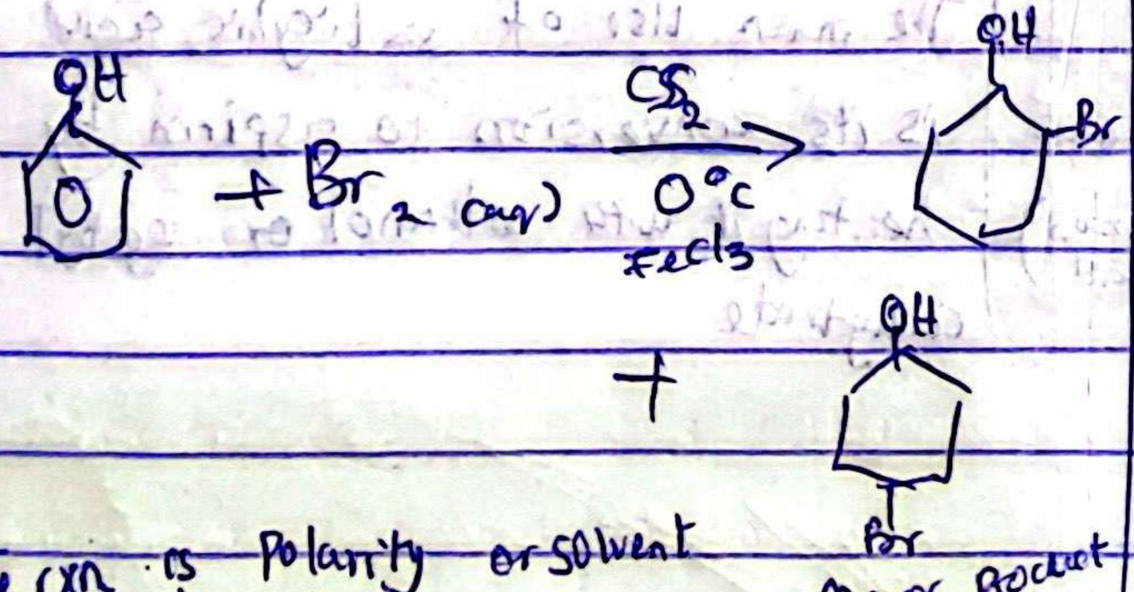


The product is temperature dependent. Raising the temperature of the ortho product to 100°C will yield the para product

(iii) Halogenation: Phenol reacts with aqueous solution of halogens to give polysubstituted product



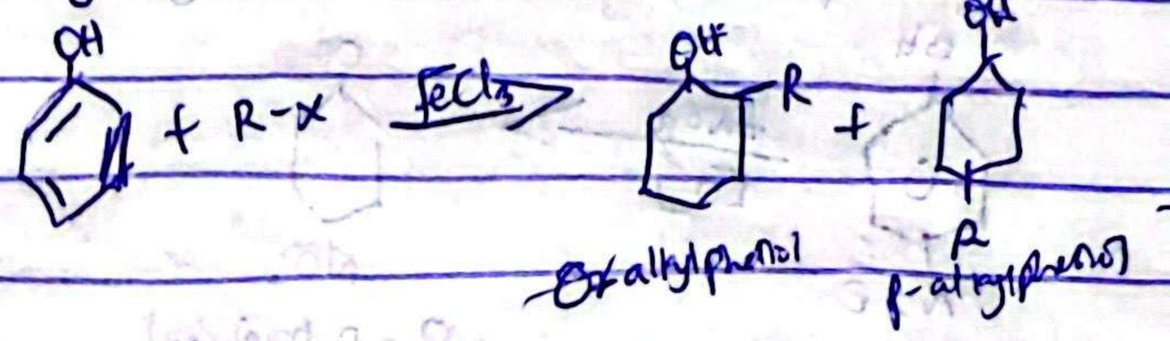
If the reaction is carried out in a solvent of low polarity such as CS_2, CCl_4 and chloroform ($CHCl_3$) the reaction can be limited to monohalogenation



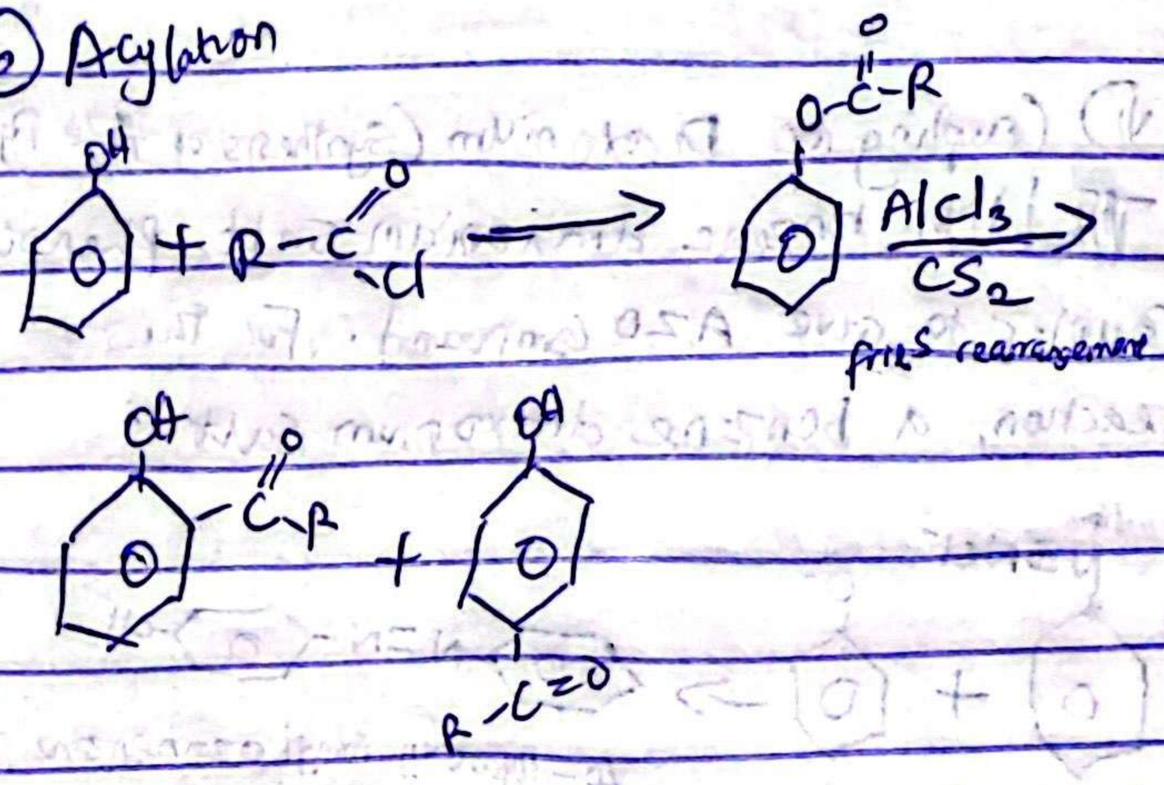
The rxn is Polarity or solvent dependent.

(iv) Friedal-Crafts Alkylation/Acylation

(a) Alkylation



(b) Acylation



Acylation is used for the preparation of phenolic ketones and this preparation occurs by means of fries rearrangement instead of direct substitution on the ring.

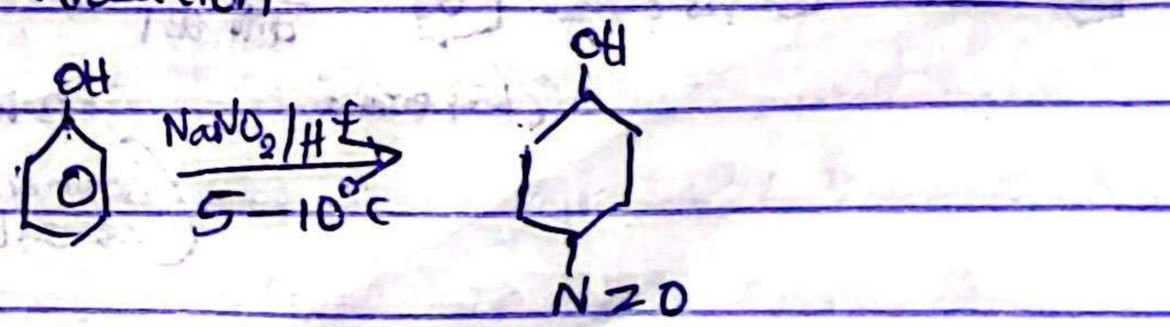
It goes through two steps;

(i) formation of phenyl ester

(ii) migration of the acyl group from the phenolic oxygen to ortho and para position of the ring.

The rearrangement appears to involve generation of acylium ion ($R-\overset{O}{\overset{\|}{C}}^{+}$) which then attack the ring, as in ordinary friedel Craft reaction

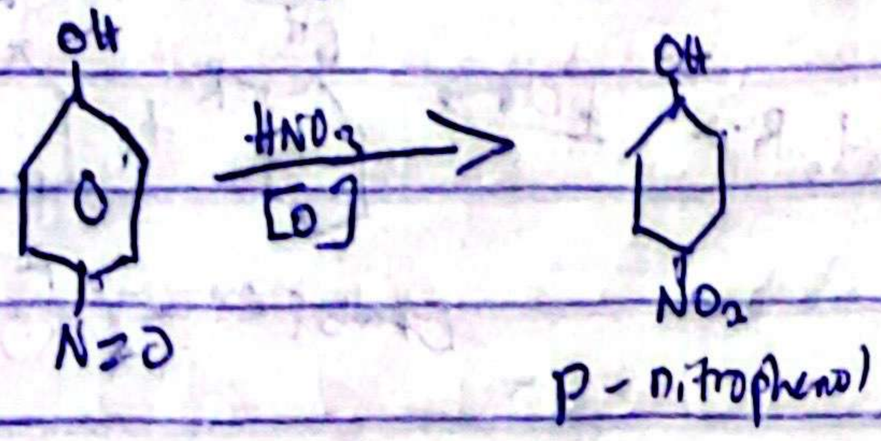
(v) Nitrosation



The nitroso product is readily oxidized to

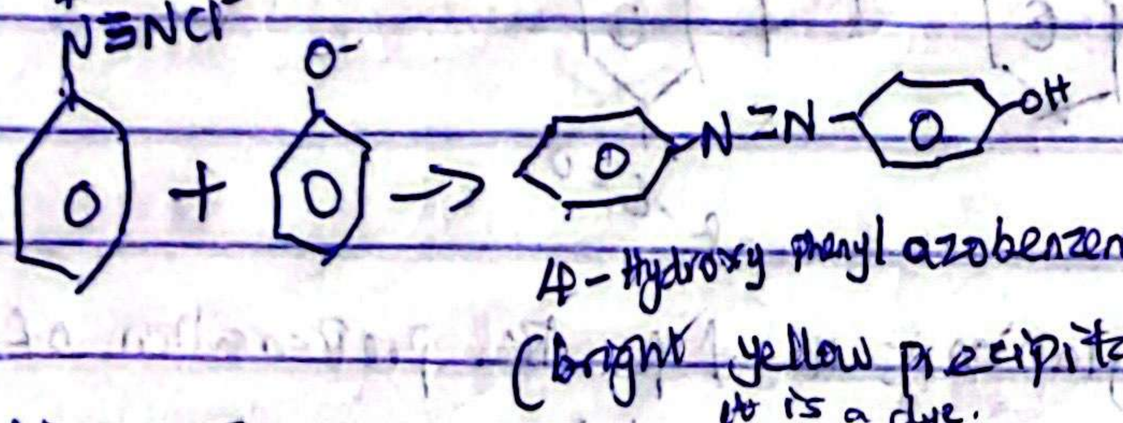
Aspirin - Acetyl Salicylic Acid

the coresponding nitro compound by HNO_3



(vi) Coupling of Diazonium (Synthesis of Azo Dyes)

The With benzene diazonium salt, Phenols couples to give AZO compound. For this reaction, a benzene diazonium salt

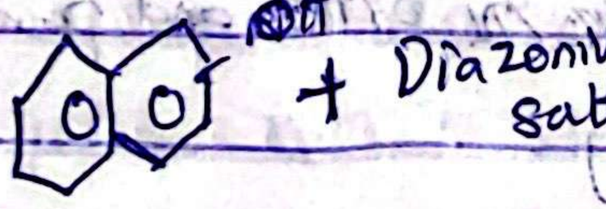


Note: In preparation of dye

Any phenol + Diazonium salt → dye

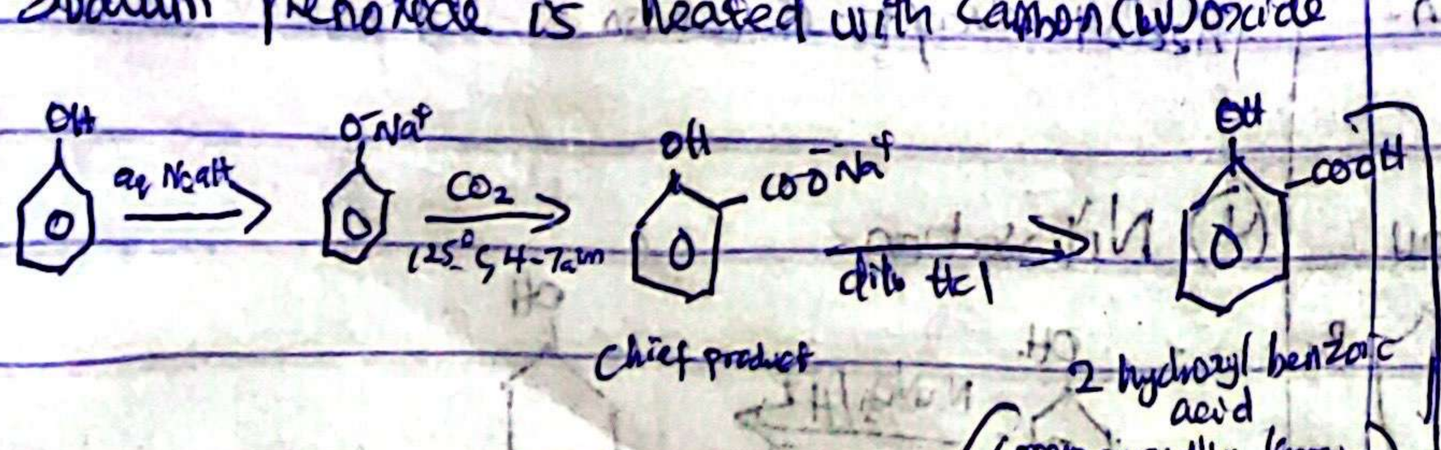
This reaction is very important in dye stuff industry because Azo compounds have very deep colours

Assignment



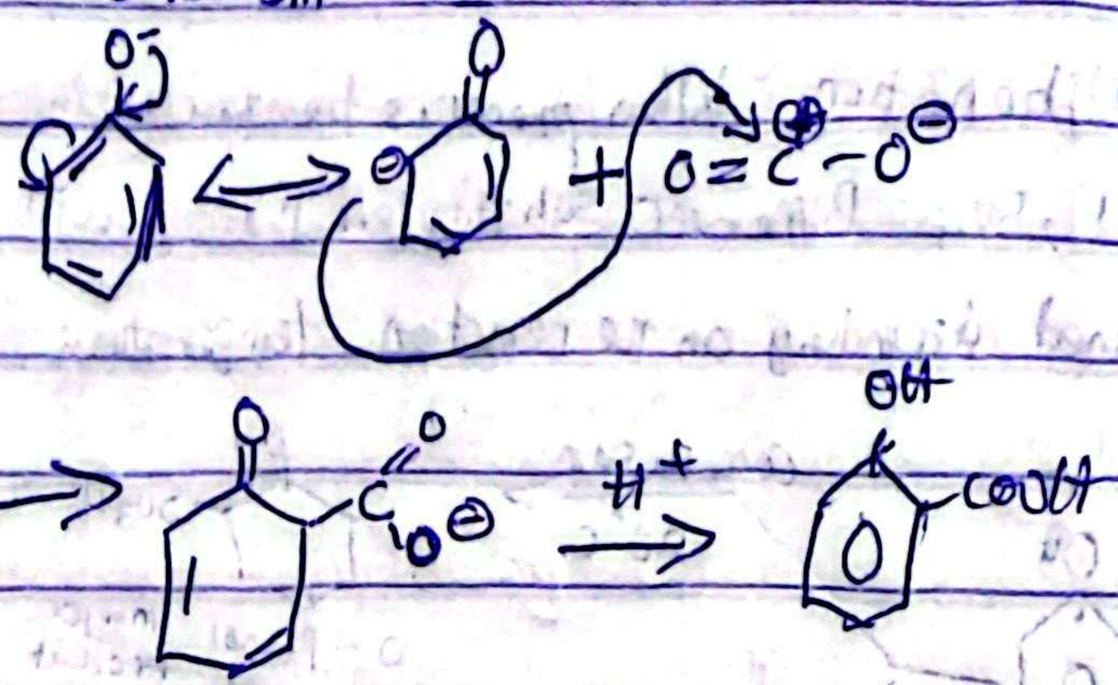
(vii) Carbonation (Kolbe Schmit reaction)

Sodium Phenoxide is heated with Carbon dioxide



The main use of salicylic acid is its conversion to aspirin by heating it with ethanol or acetyl anhydride

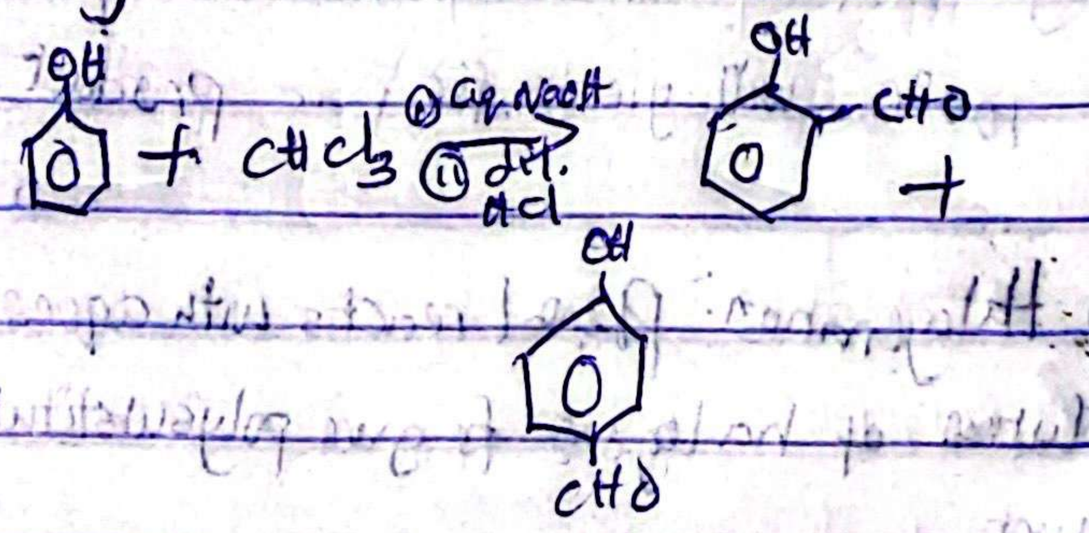
Mechanism



(viii) Aldehyde formation (Formylation)

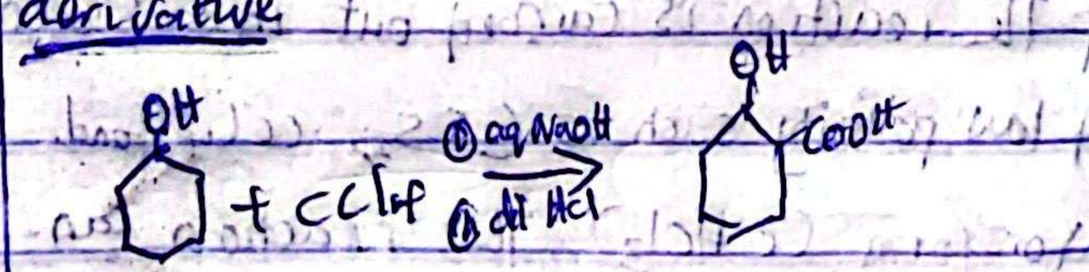
Formylation which is the introduction of -CHO group to the ring can be done in two ways

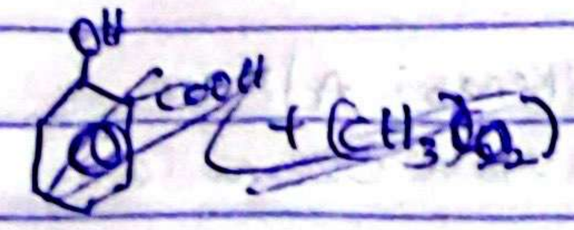
(a) By Reimer Tiemann reaction

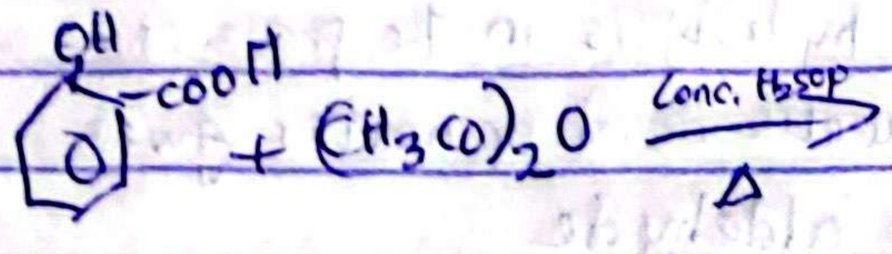


In the absence of chloroform (CCl_4) use CCl_4

Using CCl_4 instead of Chloroform, the reaction will yield carboxylic acid derivative

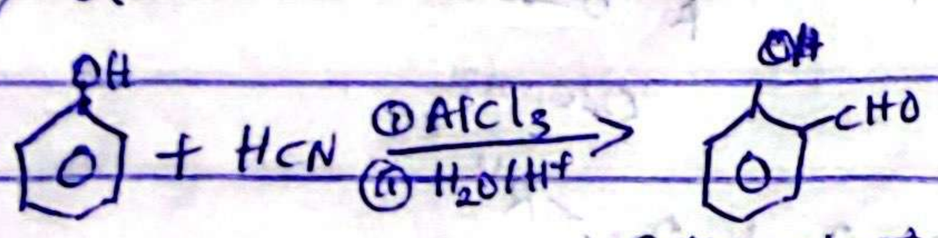






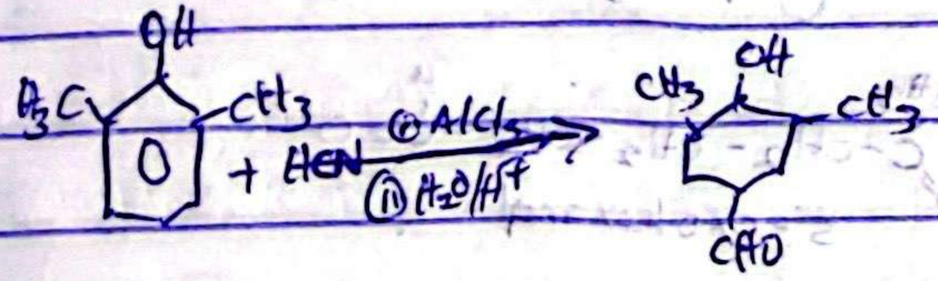
Acetyl Salicylic acid
Commonly known as aspirin

(b) Gattermann-Koch reaction



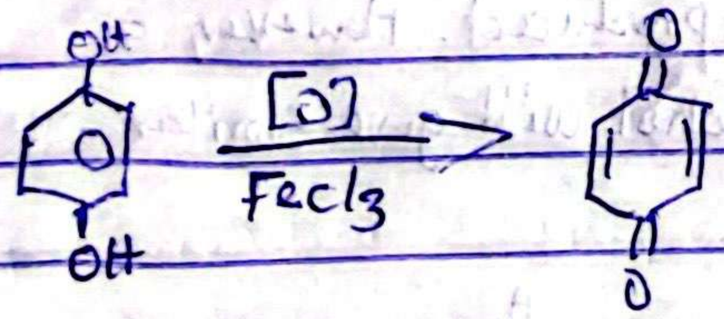
ortho - almost 100%

If the ortho position of phenol is blocked by a group, then, formylation may be caused to formed at the para position.



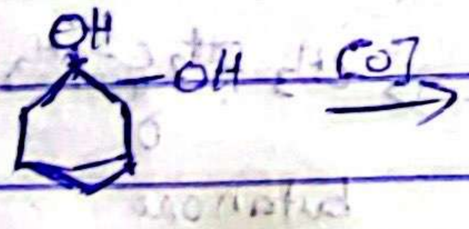
(IX) Oxidation

Phenols are easily oxidized by $FeCl_3$ or $K_2Cr_2O_7/H^+$ to quinones



1,4, benzoquinone

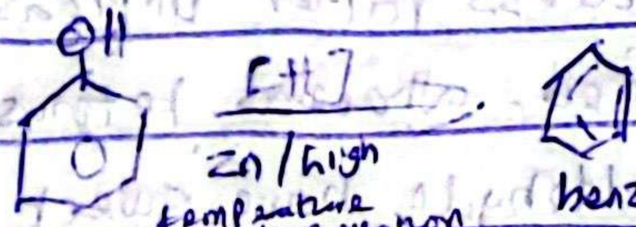
Assignment



1, 2 benzoquinone

Reduction

Phenols are reduced to the corresponding aromatic hydrocarbon by distilling it at high temperature

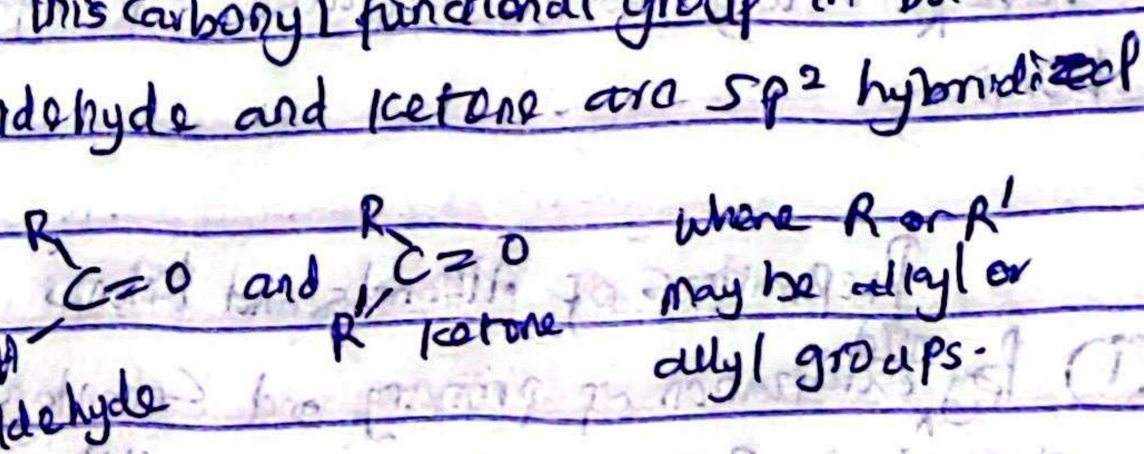


16th May, 2020

Carbonyl Compounds

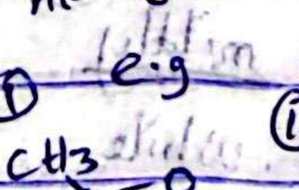
Carbonyl compounds consists of aldehydes and ketones as they both contain $\geq C=O$ functional group.

This carbonyl functional group in both aldehyde and ketone are sp^2 hybridized



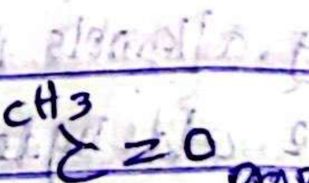
Aldehyde

(I) e.g



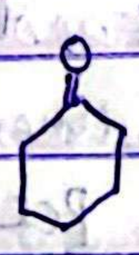
ethanal

(II)



propanone (acetone)

(III)



cyclohexanone

Therefore, they have σ and π bond.

They are generally very reactive because of the π bond and the polarization of $C=O$ bond. However, aldehydes are generally more reactive, being more easily oxidized and also more susceptible to nucleophilic addition reaction i.e electrophile

Physical property of Aldehyde & Ketone

① They are mostly colourless liquid at room temperature, especially the simple aldehydes and ketone. The lower aldehydes possess rather unpleasant pungent smell, whereas ketones and also benzaldehyde have sweet odours

② The lower aldehydes and ketones are appreciably soluble (miscible) in water due largely to their ability to form hydrogen bond with the water molecule

③ The lower aliphatic aldehyde and ketones have higher boiling point because of hydrogen bonding

Preparations of Alkanals and ketones

① By mild oxidization of primary and Secondary alcohols: Primary alkanols if mildly oxidized will give aldehydes while Secondary alkanols will yield ketones However, oxidation of primary alkanols often lead to carboxylic acid when strong oxidizing agent is used, PCC or PCM is a better oxidizing agent on the conversion of alcohols

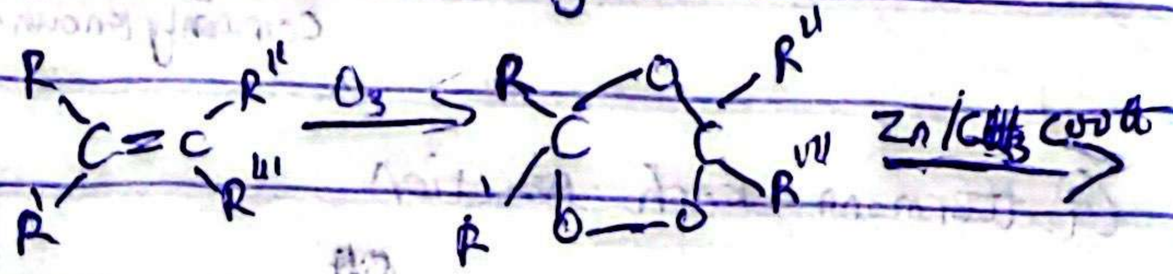
$$R-CH_2-OH \xrightarrow{PCC/PCM} R-C(=O)-H$$

1° alcohol

$$R-CH(OH)-R' \xrightarrow[[O]]{PCC/PCM} R-C(=O)-R'$$

Note interest

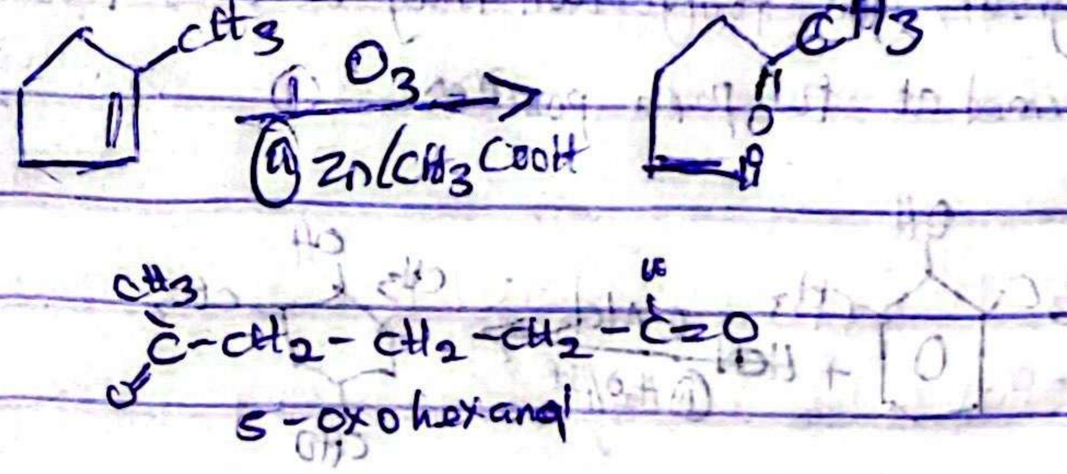
② By ozonolysis of Alkenes: Alkenes reacts with ozone to form ozonide which on hydrolysis in the presence of zinc/acetic acid or water gives ketone or aldehyde



Ozonide

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!C=O + O=C\!\!<\!\!\begin{matrix} R'' \\ R''' \end{matrix}$$

e.g



$$\begin{matrix} CH_3 \\ \\ \end{matrix}\!\!>\!C-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}=O$$

5-oxohexanal

③ Catalytic hydrogen of alkanol: When vapour of primary alcohol is passed over heated copper, a corresponding aldehyde is produced. However a secondary alcohol will give similar reaction.

$$H-CH_2-OH \xrightarrow[300^\circ C]{Cu} \begin{matrix} H \\ H \end{matrix}\!\!>\!C=O + H_2$$

1° alcohol

$$CH_3-CH_2-\underset{OH}{CH}-CH_3 \xrightarrow{''} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

2° alcohol
butan-2-ol

butanone
(ketone)

(4) Reduction of Acyl Chloride (For aldehydes only): Ketones can not be prepared with this method. Acyl chloride is hydrogenated in the presence of Pd supported over $BaSO_4$. In practice, the Pd catalyst is poisoned with sulphur to prevent the reduction process from going to alcohol.

$$R-\underset{\underset{Cl}{|}}{\overset{\overset{O}{\|}}{C}} \xrightarrow{Pd/BaSO_4} R-\underset{H}{\overset{\overset{O}{\|}}{C}}$$

acyl chloride

This reaction is referred to Rosenmond reduction

(5) Hydration of Alkyne: Methyl ketones can be prepared by hydration of terminal alkynes in the presence of Mercury salt as catalyst

$$CH_3C\equiv CH + H_2O \xrightarrow[\text{(ii) } H_2SO_4]{\text{(i) } HgSO_4} \underset{\text{enol (very stable)}}{CH_3C(OH)=CH_2} \longrightarrow CH_3\overset{\overset{O}{\|}}{C}-CH_3$$

$$HC\equiv CH + H_2O \xrightarrow[H^+]{Hg^{2+}} \underset{\text{(ethanol)}}{H-C(OH)=CH_2} \longrightarrow H-\overset{\overset{O}{\|}}{C}-CH_3$$

(aldehyde)

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