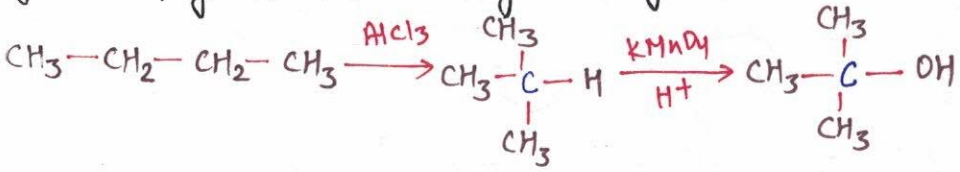
Alcohols & Phenols

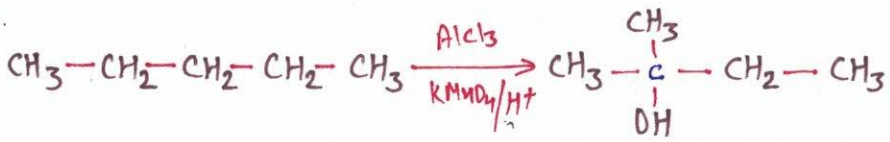
ALCOHOLS THEORY

ALCOHOLS

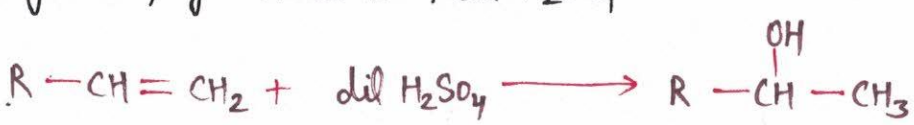
PREPARATION

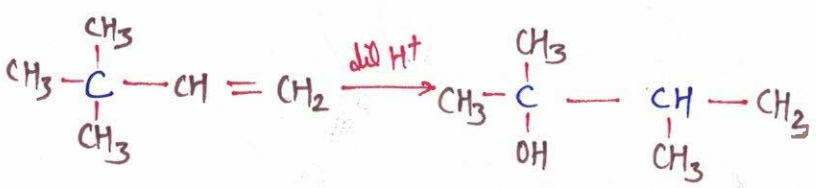
1. By oxidation of alkanes containing tertiary carbon

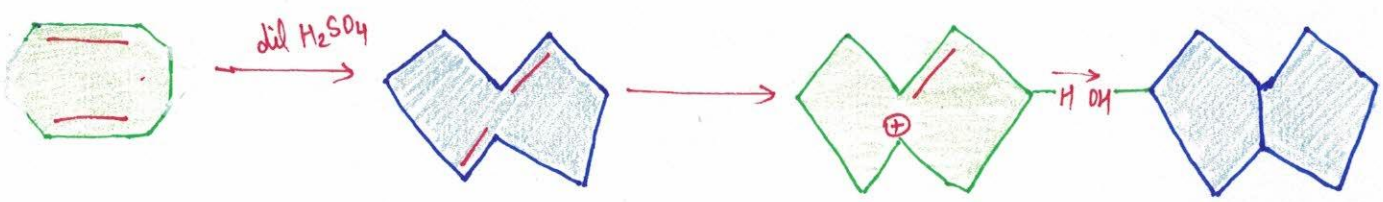




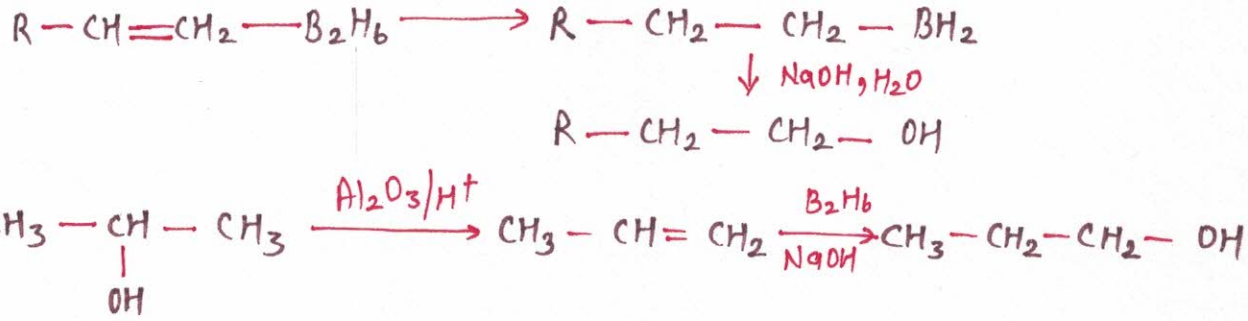
2. Hydration of alkenes with dil H_2SO_4



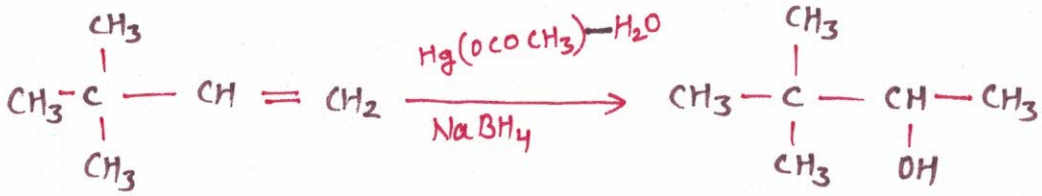




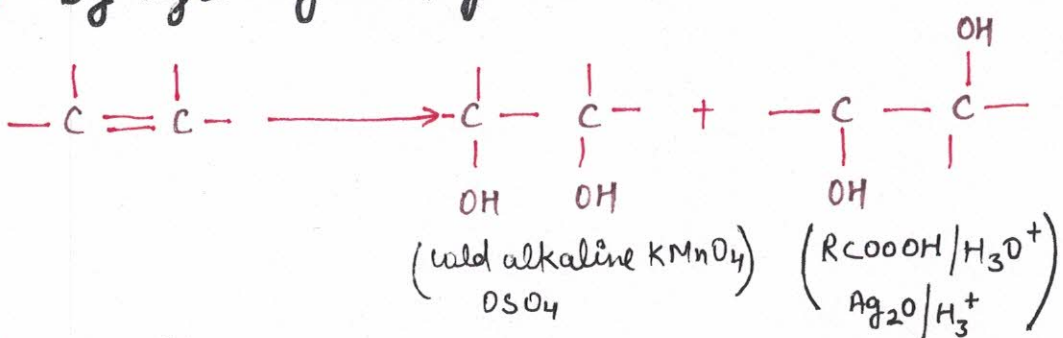
3. By hydroboration & oxidation



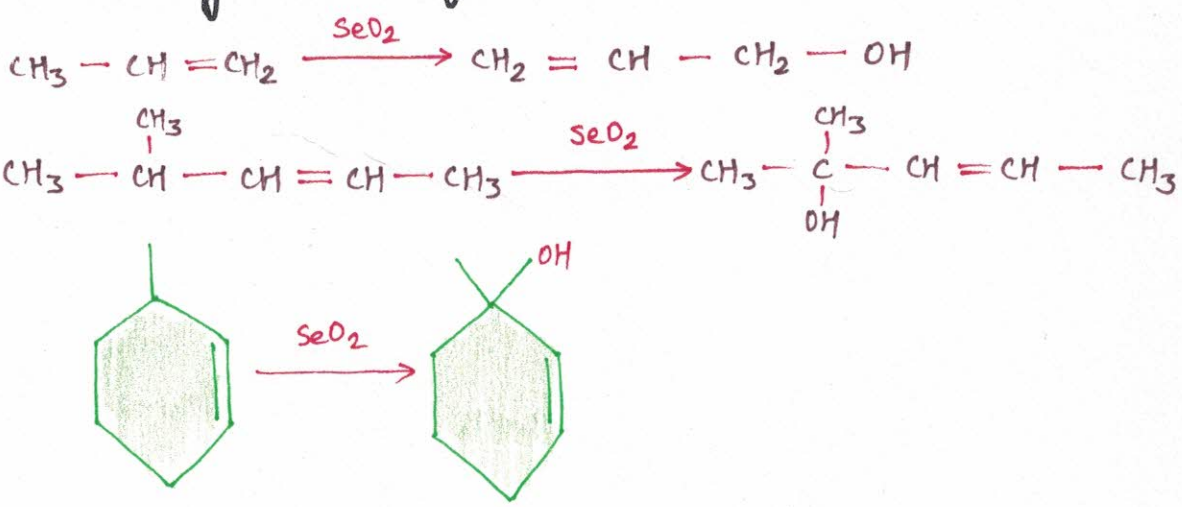
4. By oxymercuration & demercuration



5. By hydroxylation of alkenes



6. Oxidation of alkenes by SeO_2



7. By hydrolysis of alkyl halides

8. By reaction of $R\,NH_2$, $Ar\text{-}NH_2$ & $NaNO_2$ + dil HCl

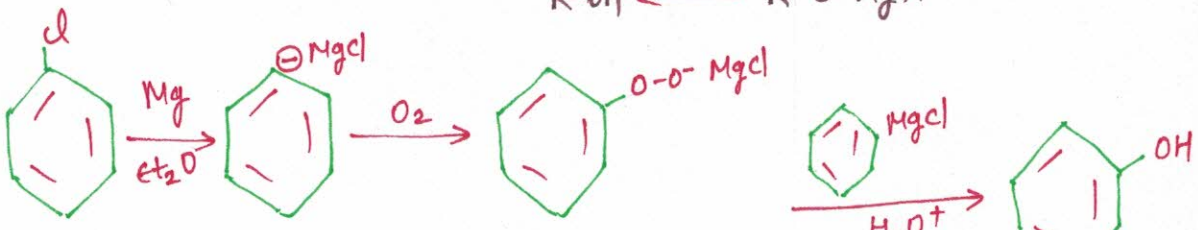
$$R-NH_2 + NaNO_2/HCl \longrightarrow R-N\equiv N^{\oplus} \xrightarrow[H_2O]{} R-OH$$

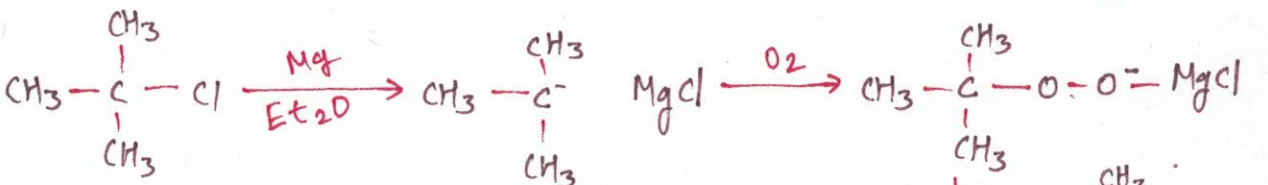
9. From Grignard Reagent

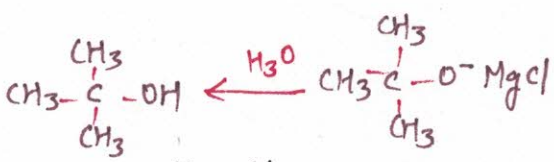
@. Conversion of $R-H / R-X \longrightarrow R-OH$

$$R-H \xrightarrow[h\nu]{X_2} R-X \xrightarrow{Mg/EC_2O} R\,MgX \xrightarrow{O_2} P-O-O^- MgX$$

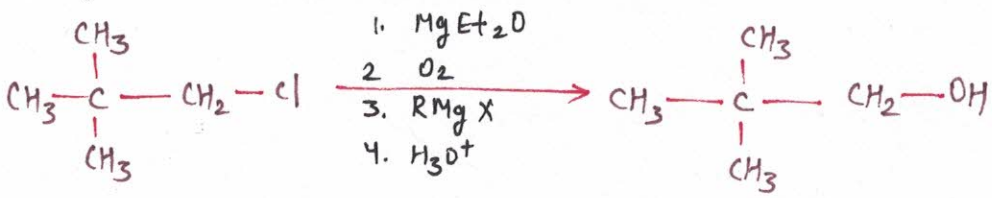
$$P-O-O^- MgX \xrightarrow{RMgX} R-O^- MgX \xrightarrow{H_3O^+} R-OH$$

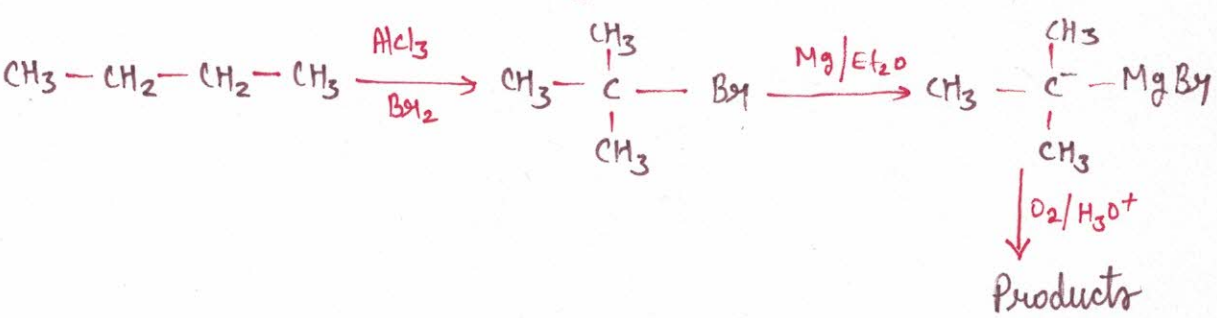






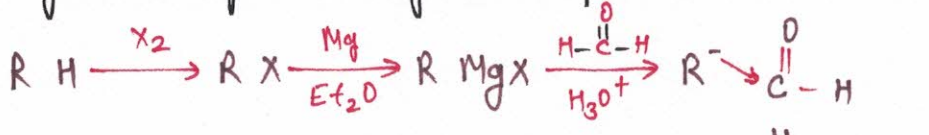
In any process in which substitution is difficult, we use grignard reagent.

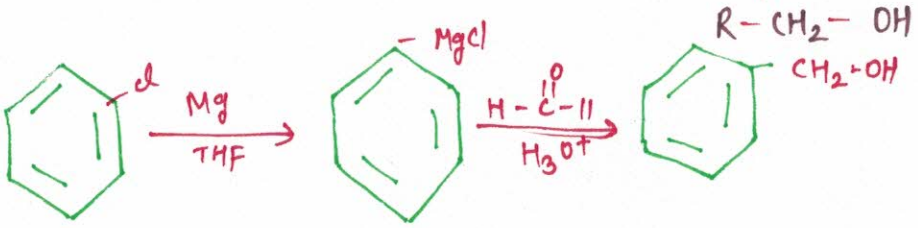


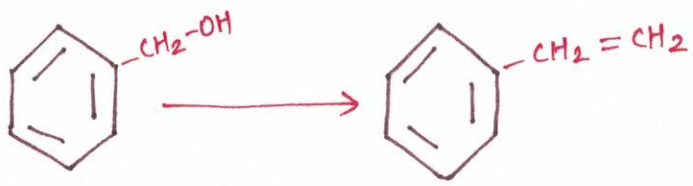


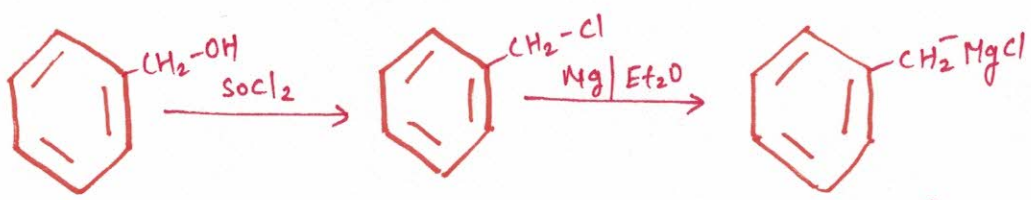
(b) Conversion of $R-X \longrightarrow R-CH_2-OH$

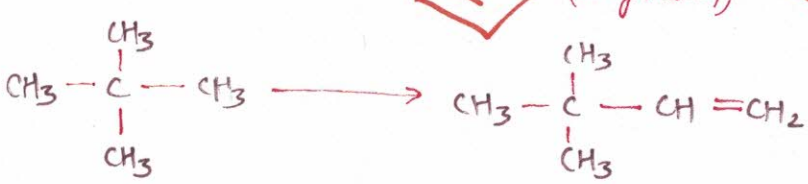
Grignard reagent undergo nucleophilic addition with carbonyls.

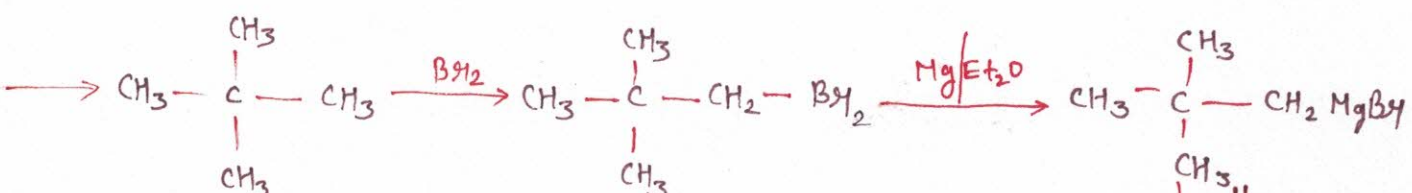


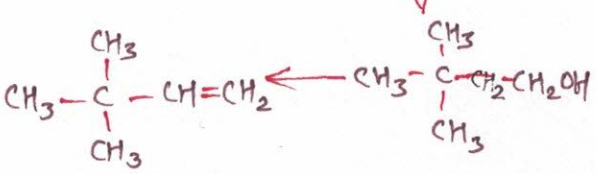


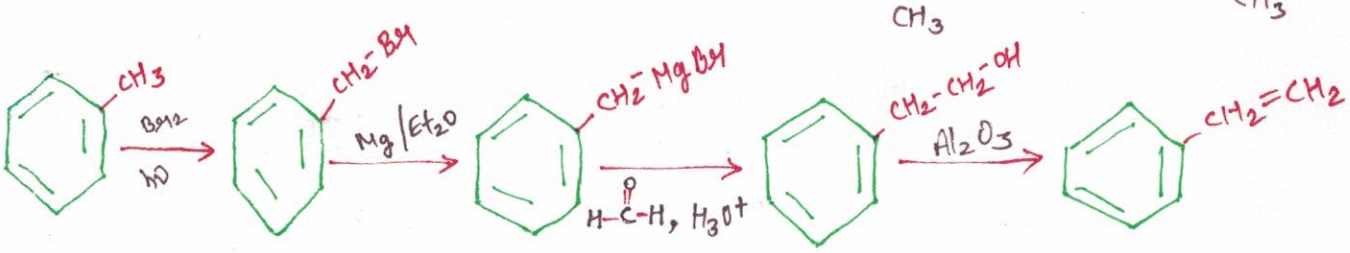


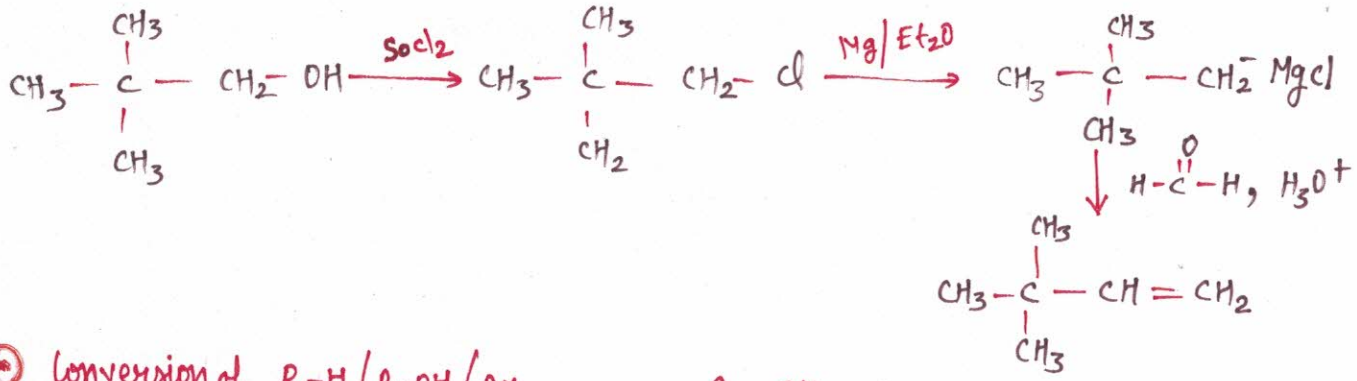


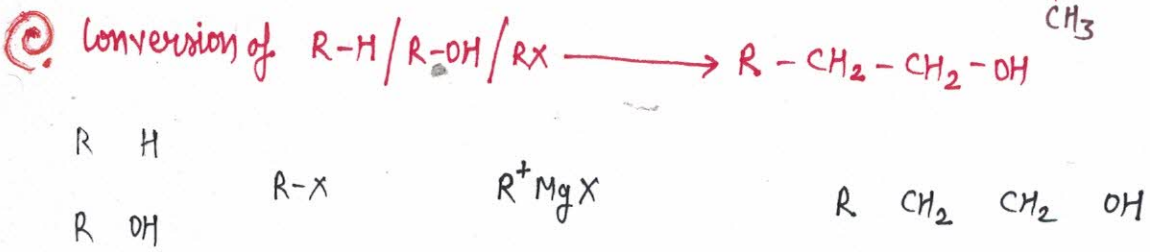


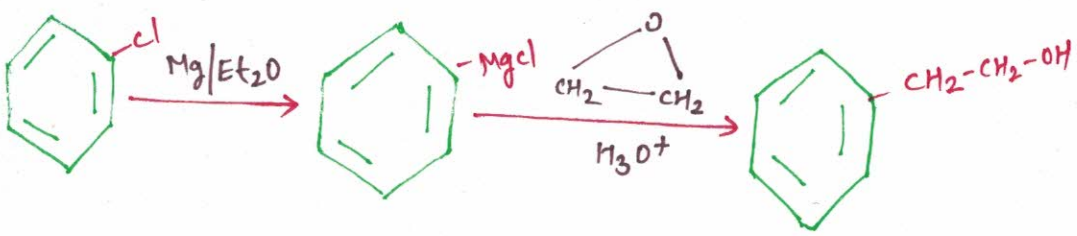


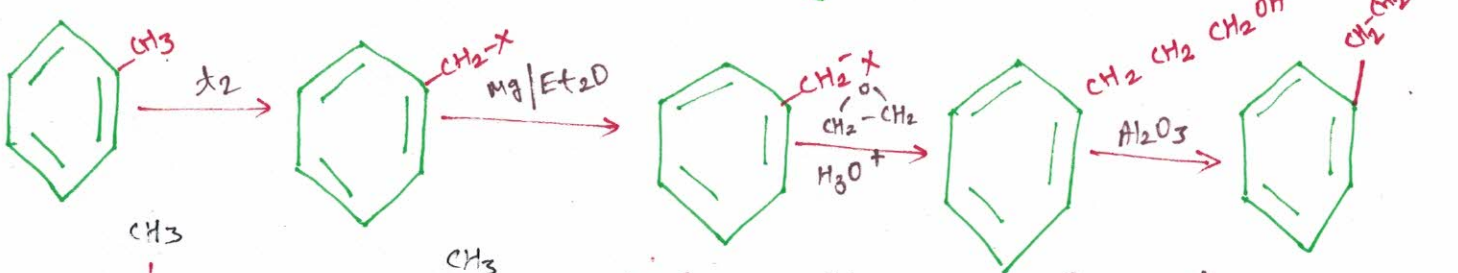


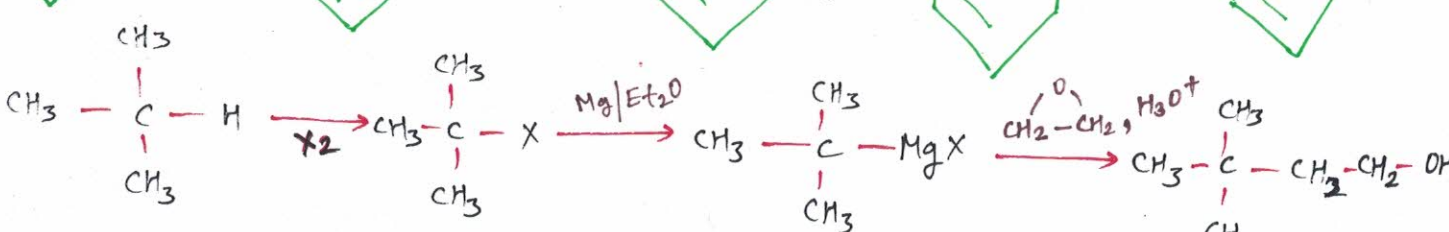


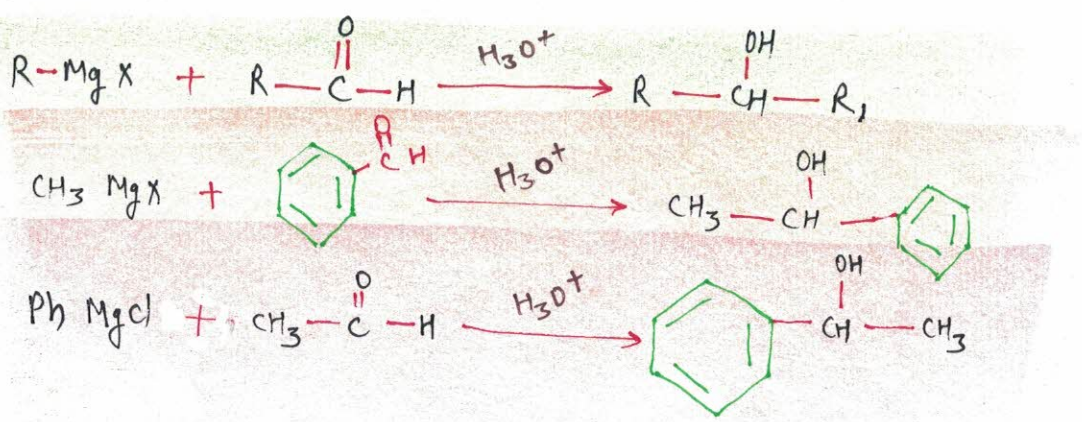




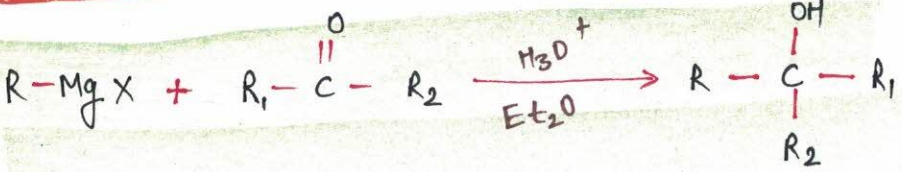




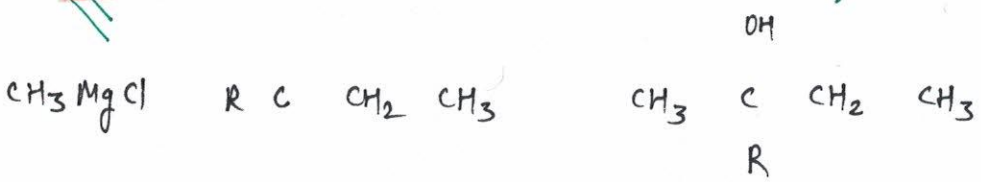


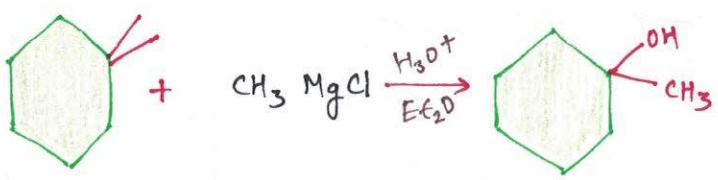


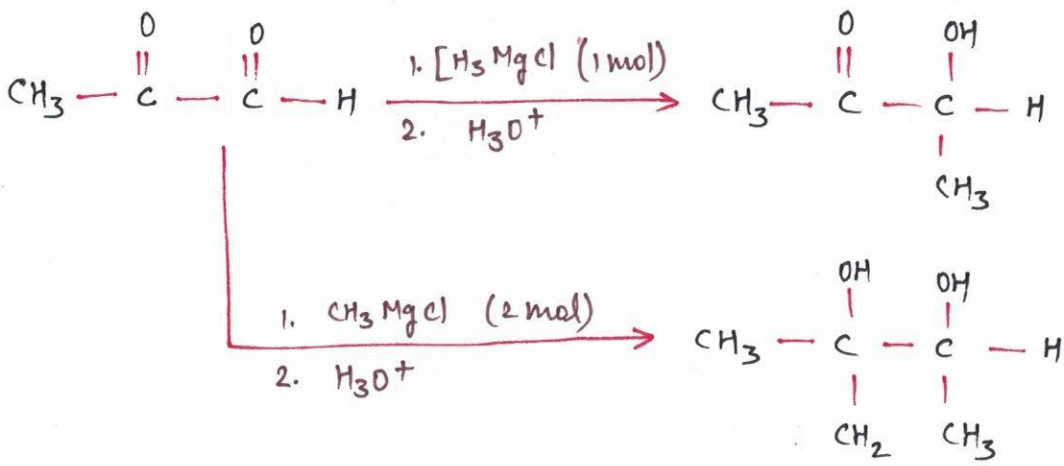
Reaction of RMgX with ketones

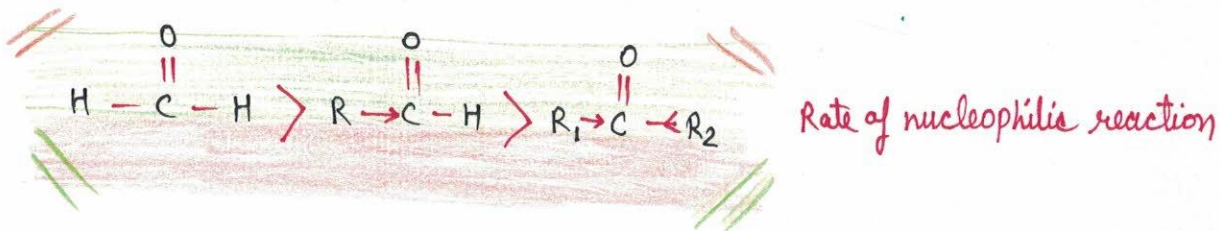


With formaldehyde → Primary alcohol
other aldehyde → Secondary
ketone → Tertiary



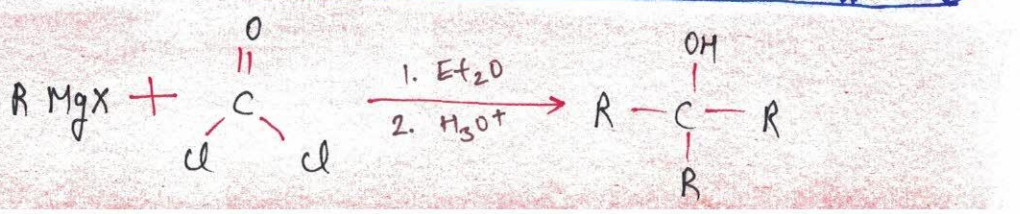




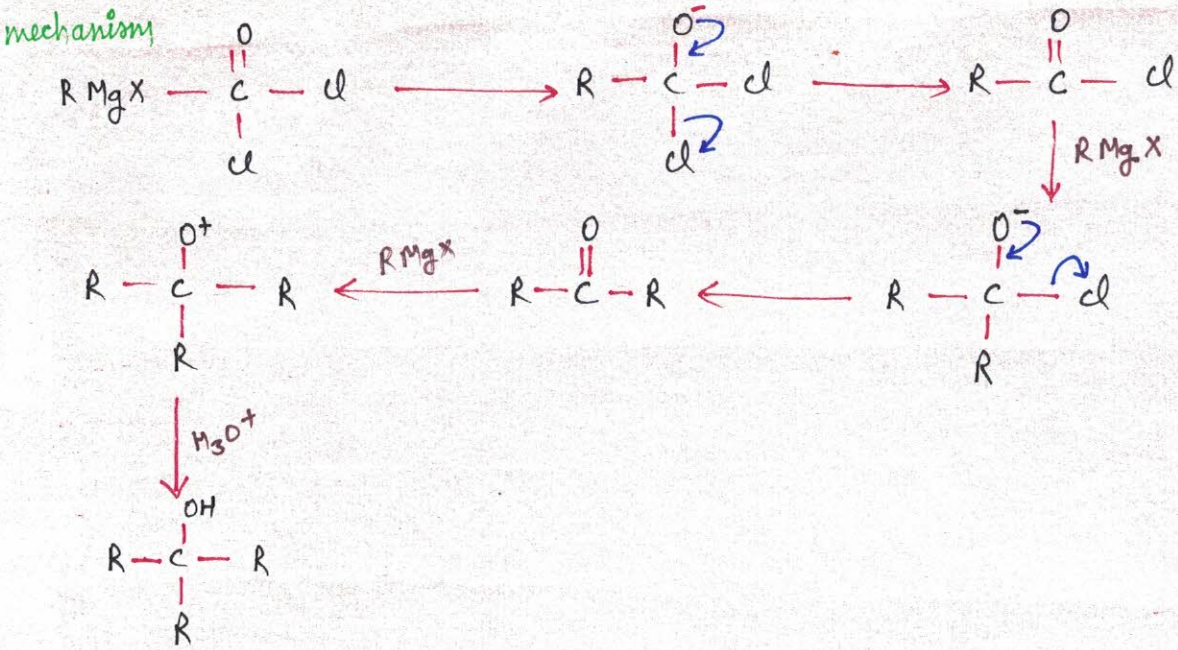


Rate of nucleophilic reaction

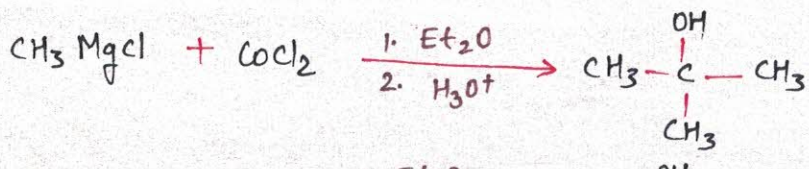
Reaction of RMgX with Phosgene ($COCl_2$)

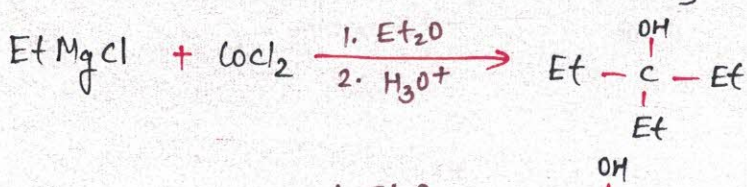


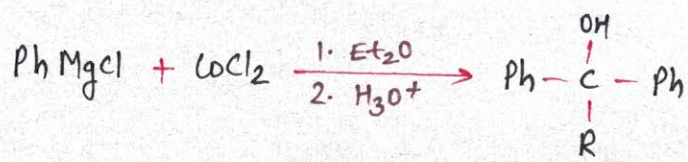
mechanism



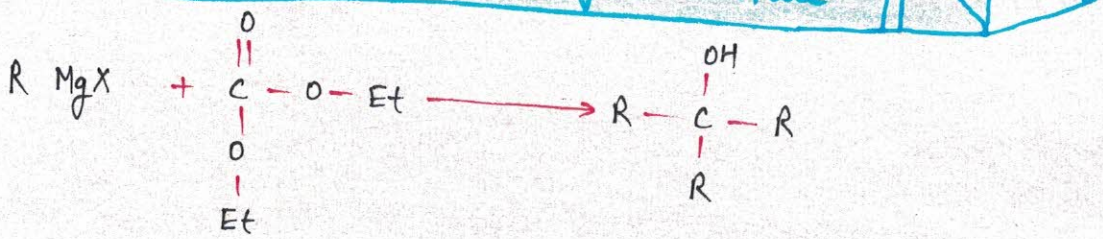
The reaction consists of two nucleophilic substitutions & one nucleophilic addition. Tri symmetrical alcohol is formed as major product.

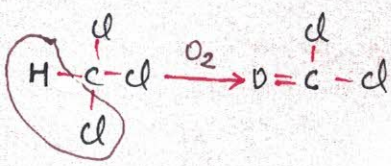




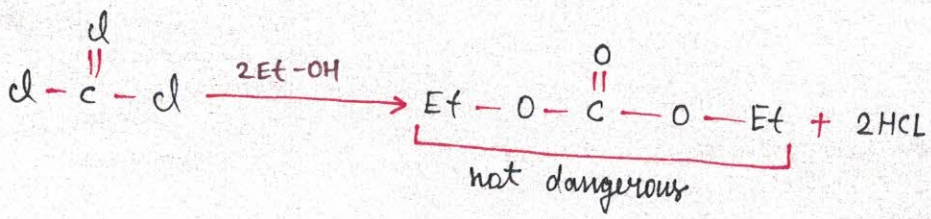


Reaction of RMgX with diethyl carbonate

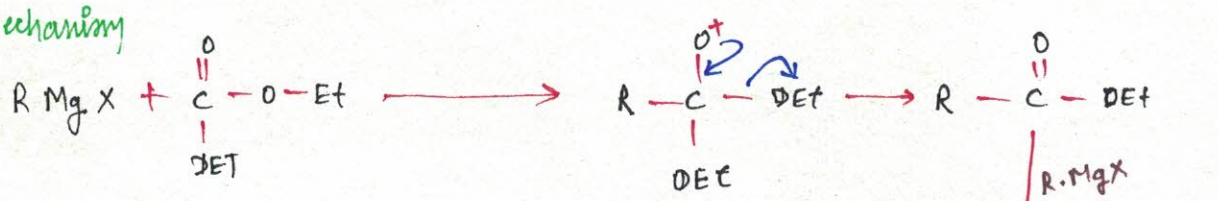


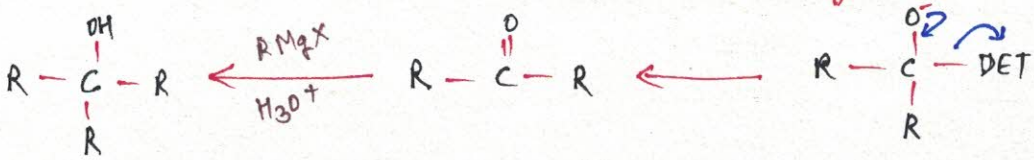
chloroform is highly dangerous in presence of O_2 because  (Phosagene) is highly dangerous.

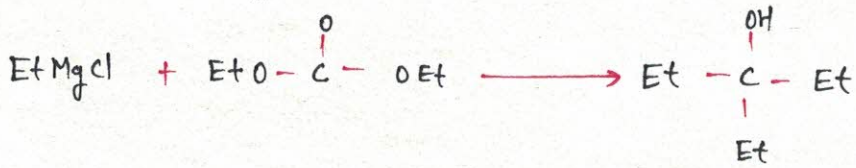
So, it is stabilised by adding Et - OH.

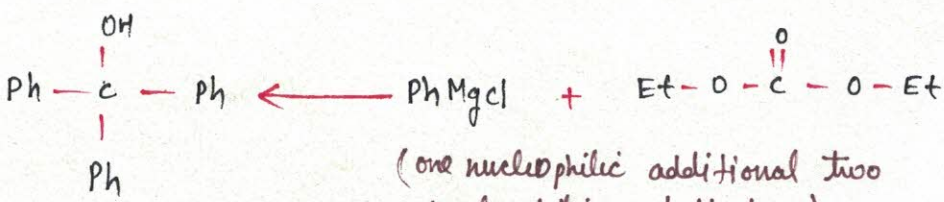


Mechanism



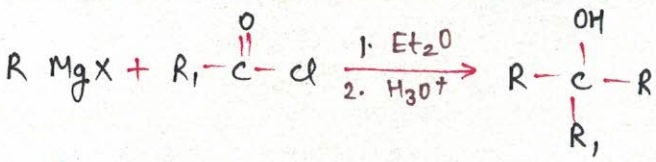




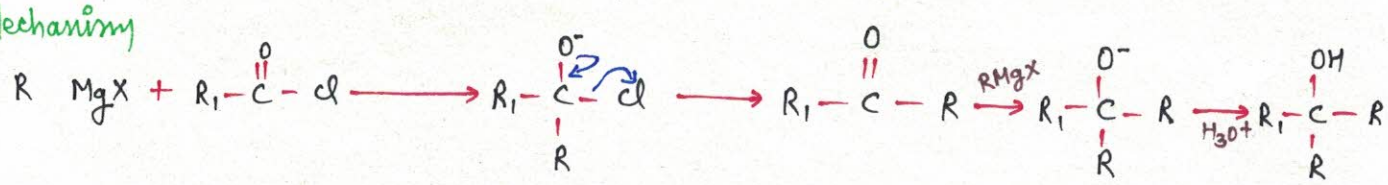


(one nucleophilic addition two nucleophilic substitution)

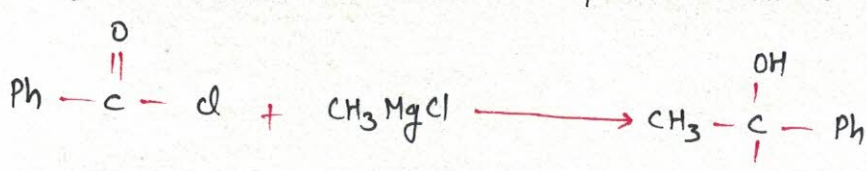
By Reaction of RMgX with acid chloride

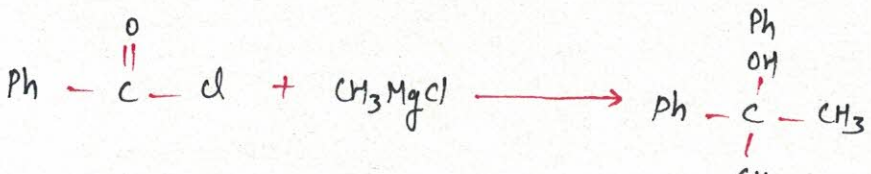


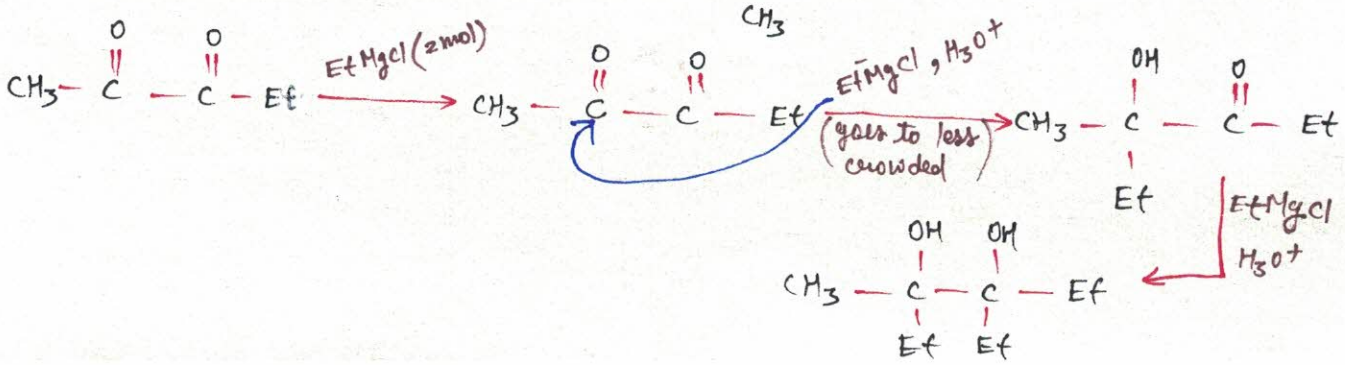
Mechanism



Disymmetrical alcohol is formed as major product. this reaction consists of one nucleophilic substitution & one nucleophilic additions.



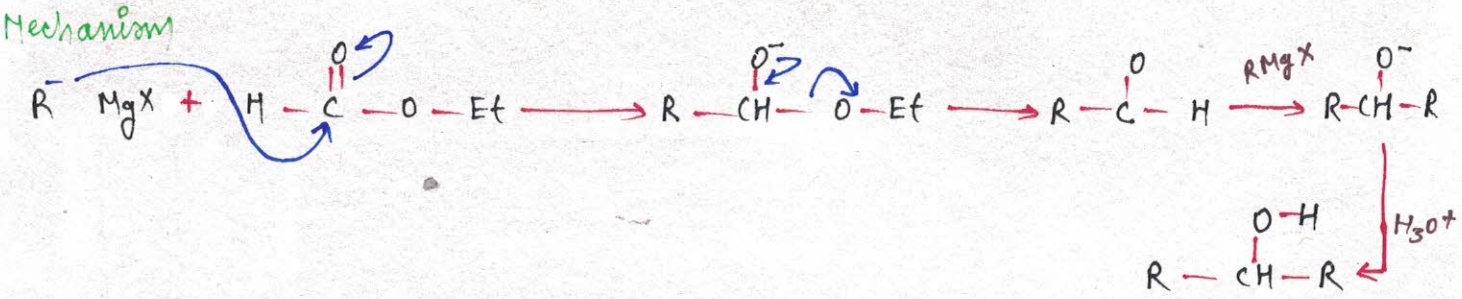




Reaction of RMgX with $H-\overset{O}{\overset{\|}{C}}-OEt$

$$R\ MgX + H-\overset{O}{\overset{\|}{C}}-O-Et \longrightarrow R-\underset{OH}{\underset{|}{CH}}-R$$

Mechanism



Disymmetrical secondary alcohol is formed one nucleophilic substitional one nucleophilic addition.

$$CH_3MgCl + HCOOEt \xrightarrow[H_3O^+]{Et_2O} CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$$

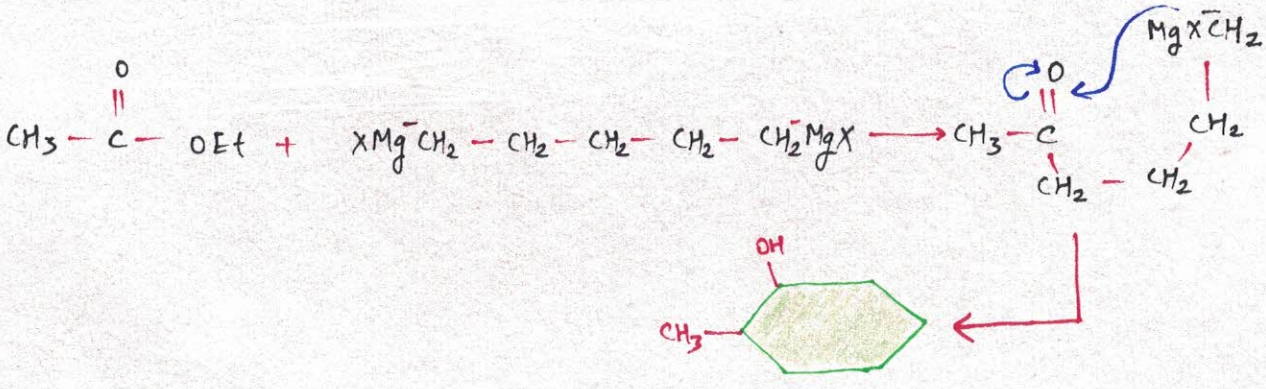
$$EtMgCl + HCOOEt \xrightarrow[H_3O^+]{Et_2O} Et-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-Et$$

$$PhMgCl + HCOOEt \xrightarrow[H_3O^+]{Et_2O} Ph-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-Ph$$

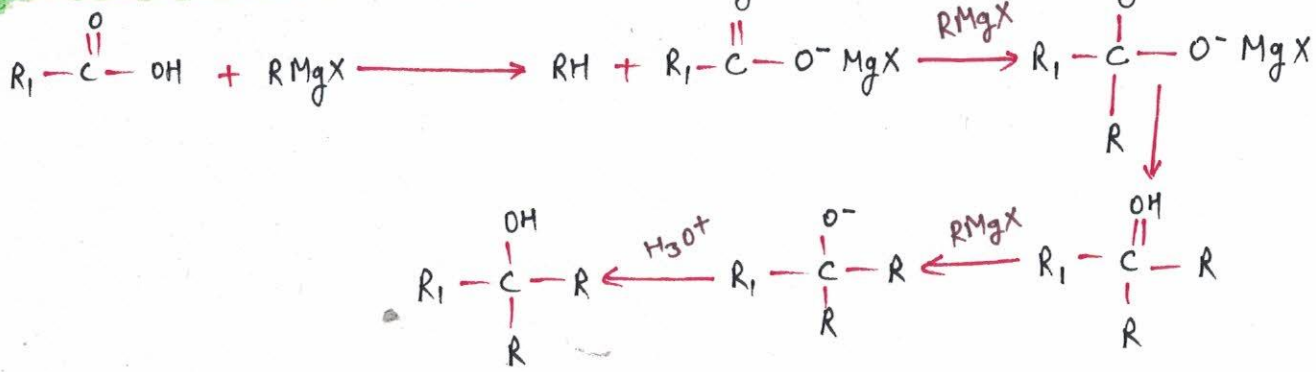
RMgX will give tertiary alcohol with $R-\overset{O}{\overset{\|}{C}}-O-E$

$$CH_3MgCl + Ph-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow[H_3O^+]{Et_2O} Ph-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$$

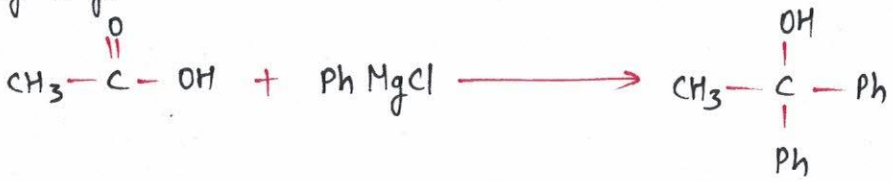
$$PhMgCl + CH_3-\overset{O}{\overset{\|}{C}}-OEt \longrightarrow CH_3-\underset{Ph}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-Ph$$

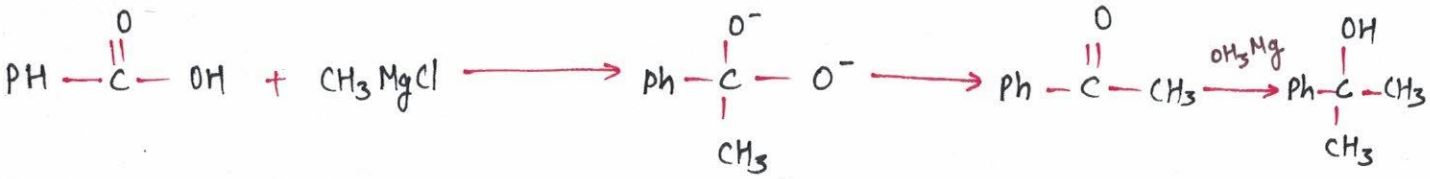


From $RMgX$ & $R_1-\overset{O}{\overset{\|}{C}}-OH$

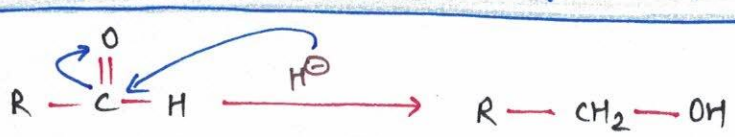


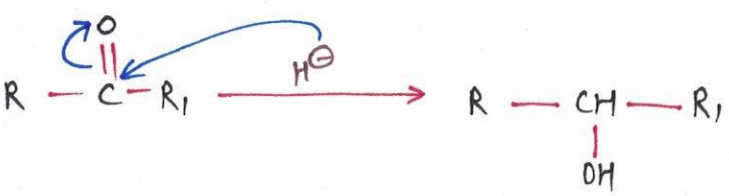
Every acid reacts with 3 mole of $RMgX$. Every acid derivation reacts with 2 mole of $RMgX$.





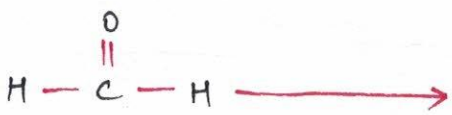
By reduction of carbonyl compounds

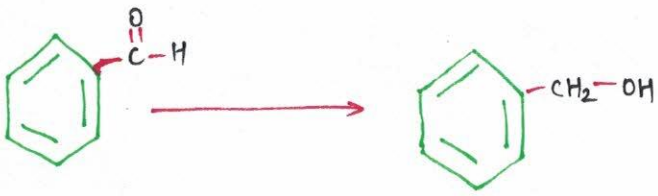




Aldehyde on reduction ⟶ Primary alcohol

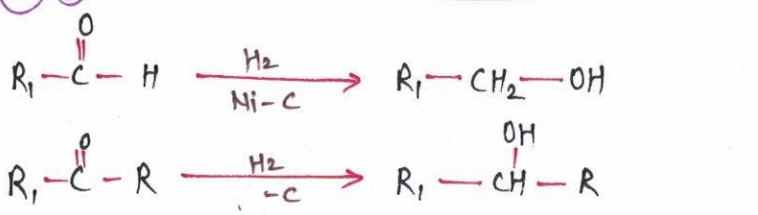
Ketone on reduction ⟶ Secondary alcohol

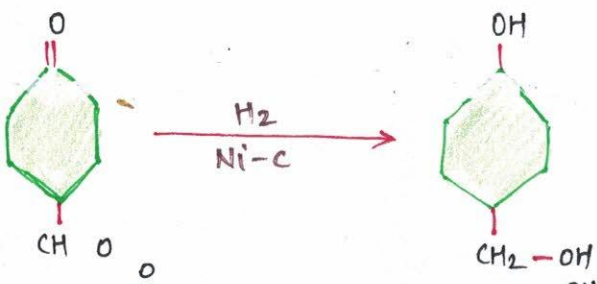


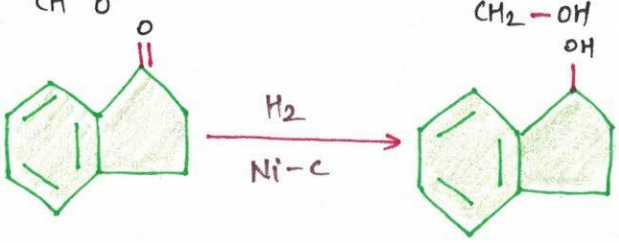


METHODS OF REDUCTION

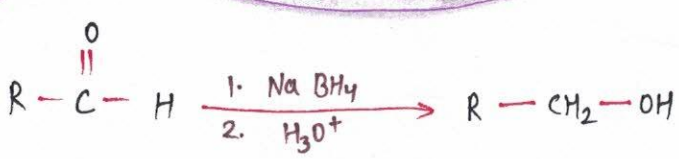
By Catalytic Hydrogenation

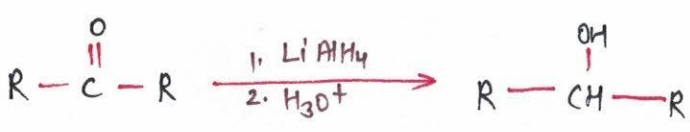




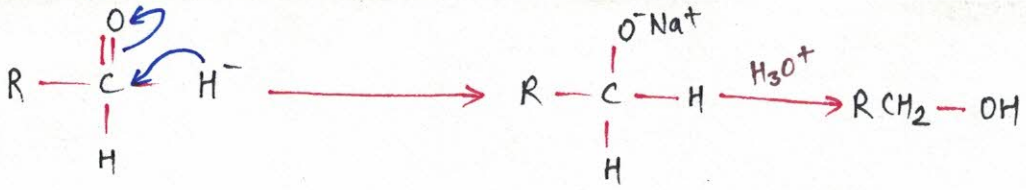


Reduction by $NaBH_4$ / $LiAlH_4$ (Give H^+)

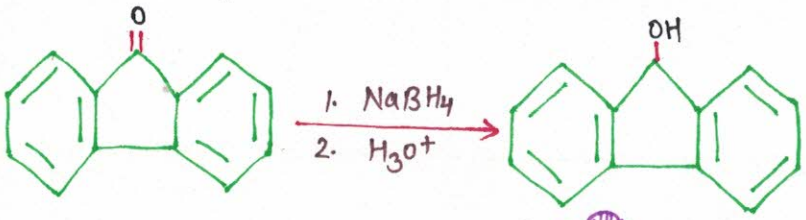




Mechanism

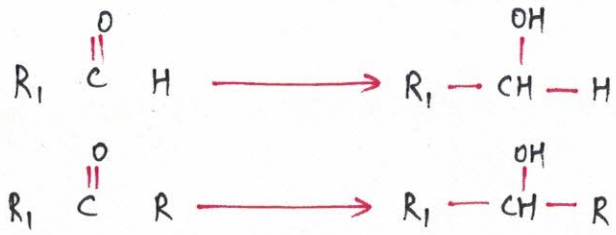


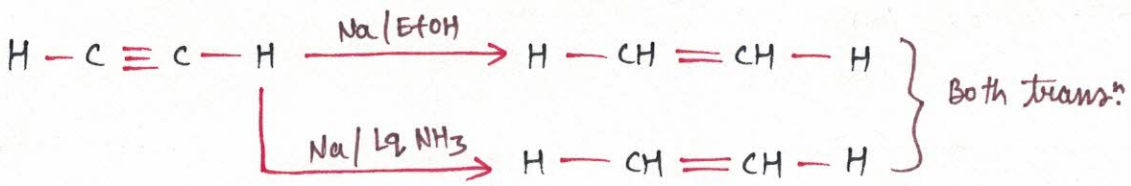
This is nucleophilic additions.



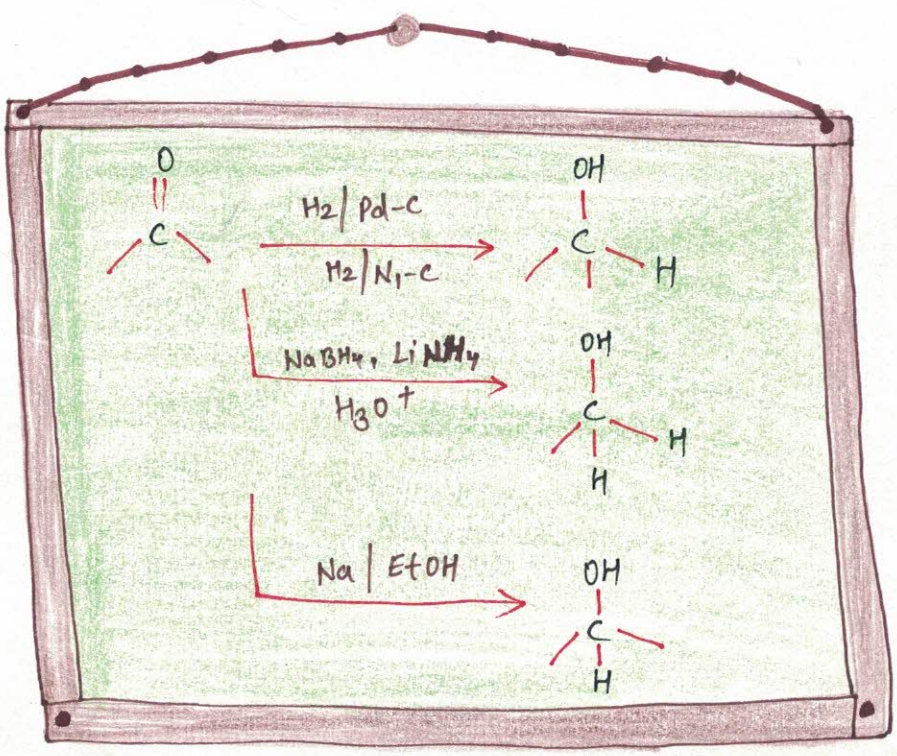
By Bouvault Blanc reduction

Na/EtOH Bouvault Blance reagent

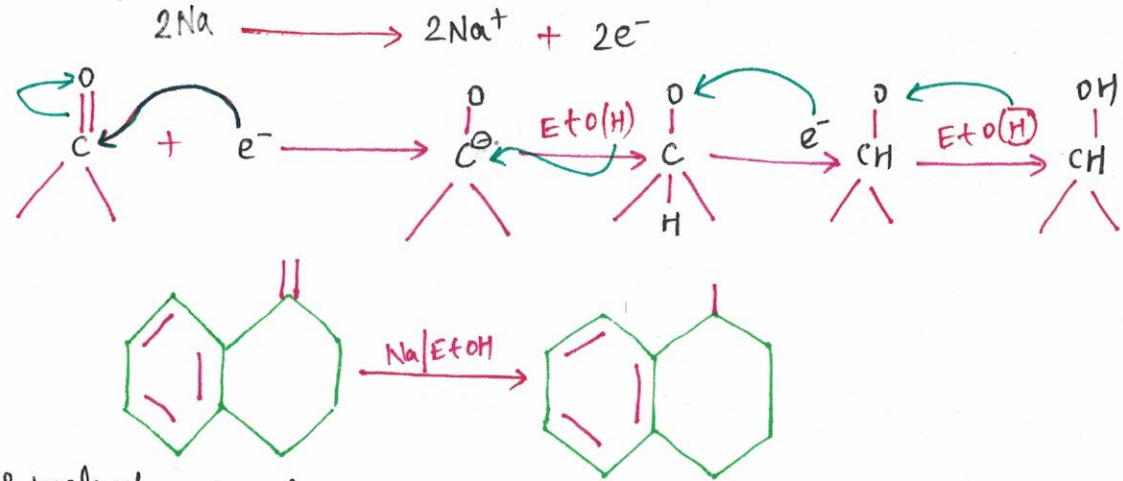




Finally,



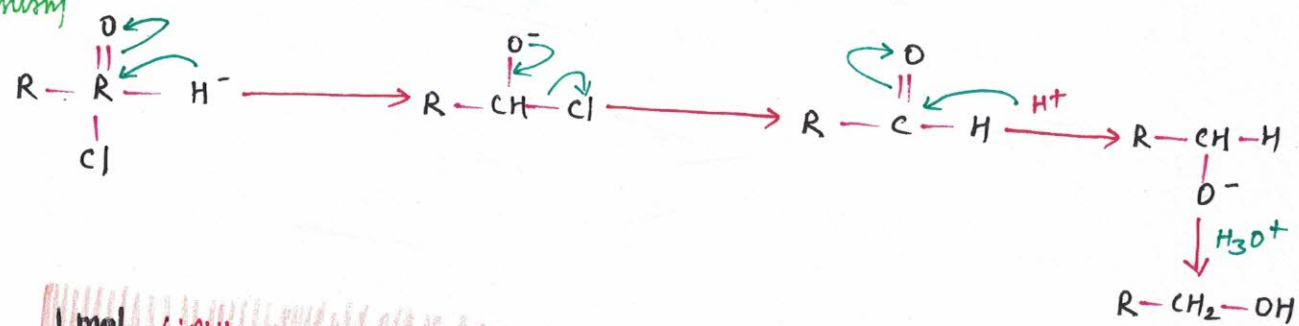
Mechanism



one mole of carbonyl requires two electrons. so, every mole of carbonyl requires two moles of Na/EtOH.

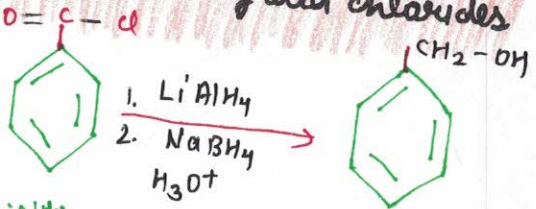
By Reduction of acid chlorides

Mechanism



1 mol $LiAlH_4 \rightarrow 4H^-$ So 1 mol $LiAlH_4$ reduces 2 mol of acid chlorides

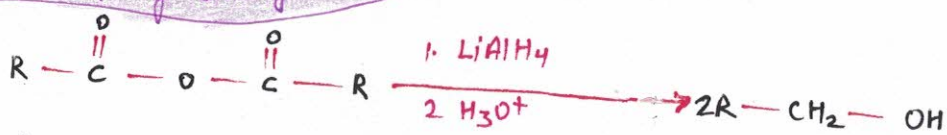
First reaction is nucleophilic substitution.
Second reaction is nucleophilic addition.



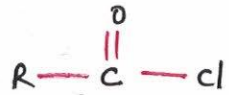
$Al_2O_3 + 3C + 3Cl_2 \rightarrow 2AlCl_3 + 3CO \xrightarrow{LiAlH_4} AlH_3 \rightarrow LiAlH_4$

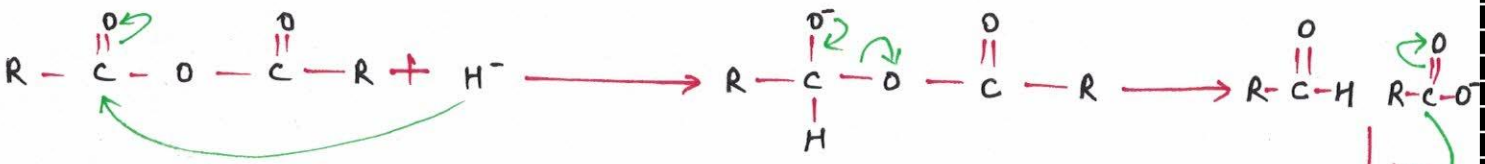
$B_2O_3 + 3C + 3Cl_2 \rightarrow BCl_3 \rightarrow B_2H_6 \xrightarrow{NaH} NaBH_4$

By reduction of anhydrides



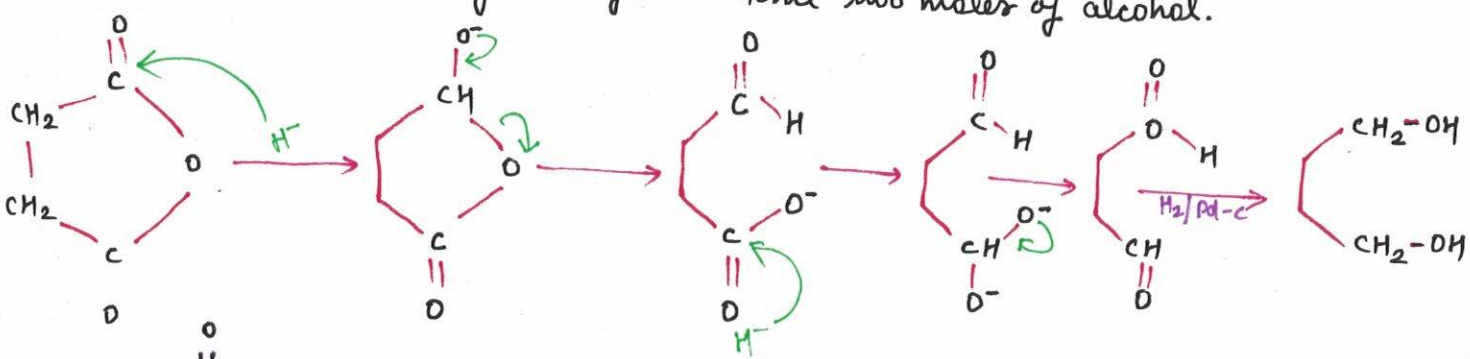
$LiAlH_4$ is more better reducing group than $NaBH_4$ because B is less electronegative than Al. Moreover $LiAlH_4$ is more ionic than $NaBH_4$ which is covalent.

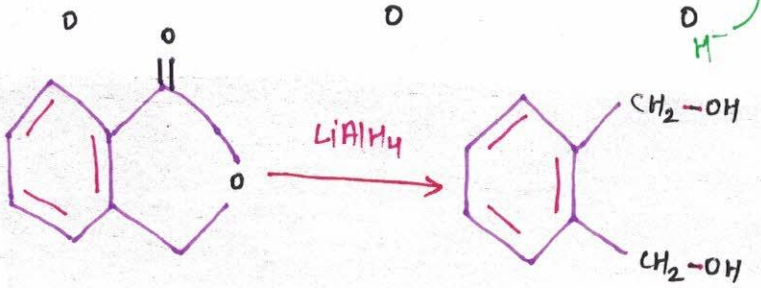
In  &  ,  & Cl^- are leaving groups, but Cl^- is better leaving group. so anhydrides can only be reduced by $LiAlH_4$ not $NaBH_4$.

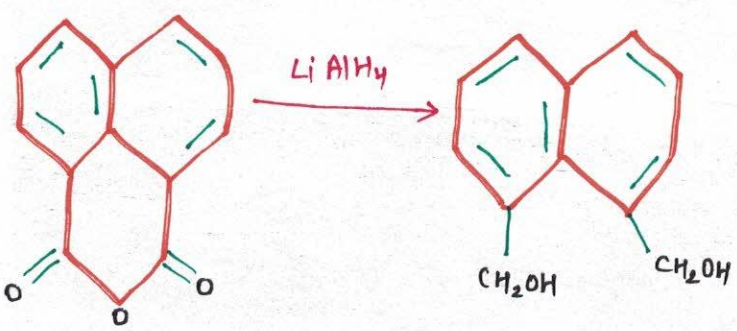


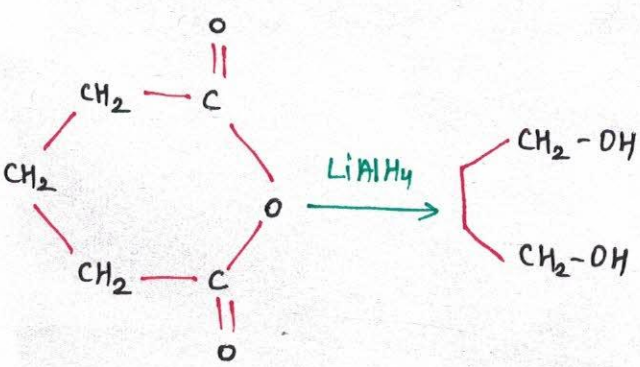
bad leaving group ← O^{-2} +

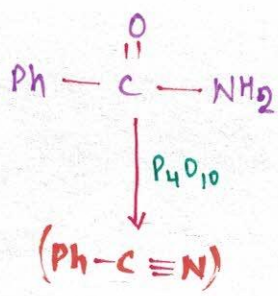
Hence, we get two moles of aldehydes & hence two moles of alcohol.



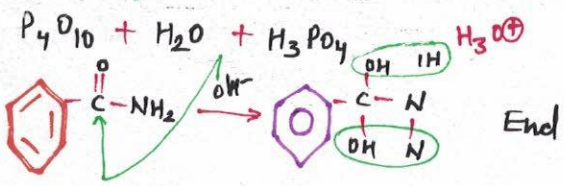








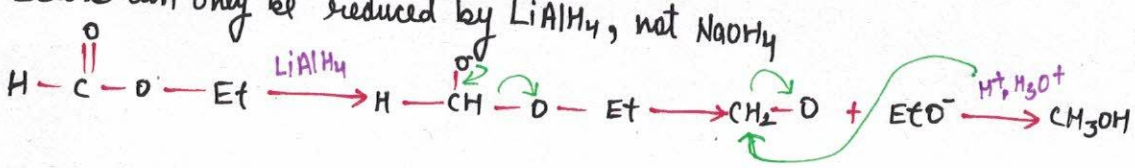
Mechanism

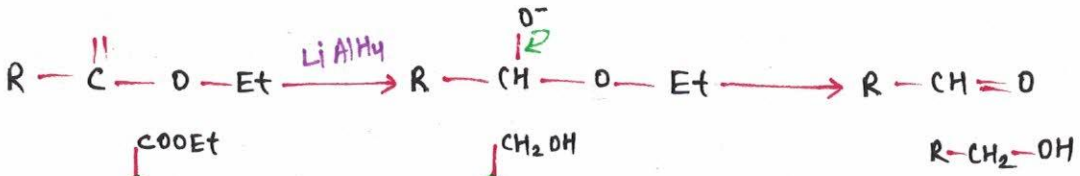


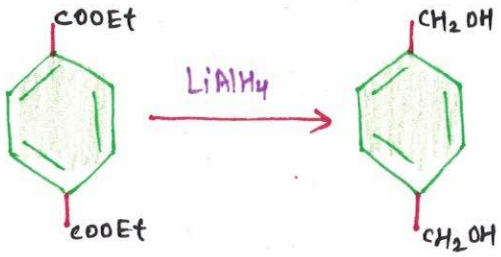
End

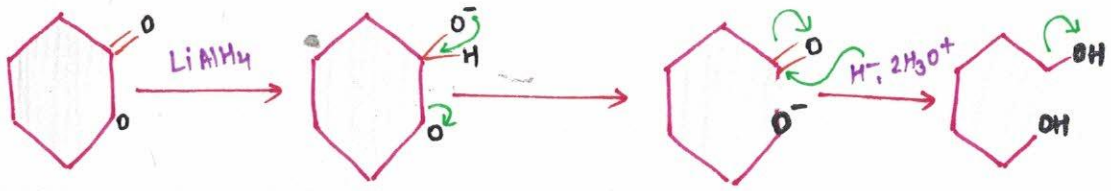
By reduction of esters

Esters can only be reduced by $LiAlH_4$, not $NaOH_4$

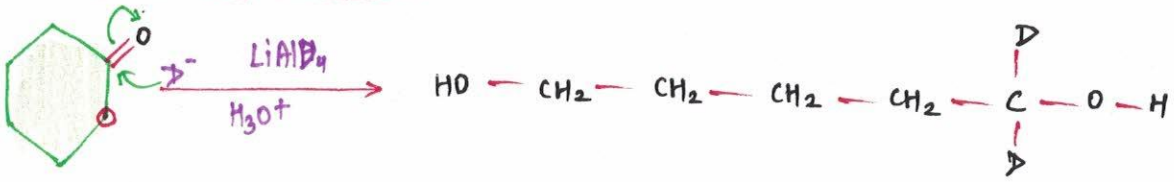


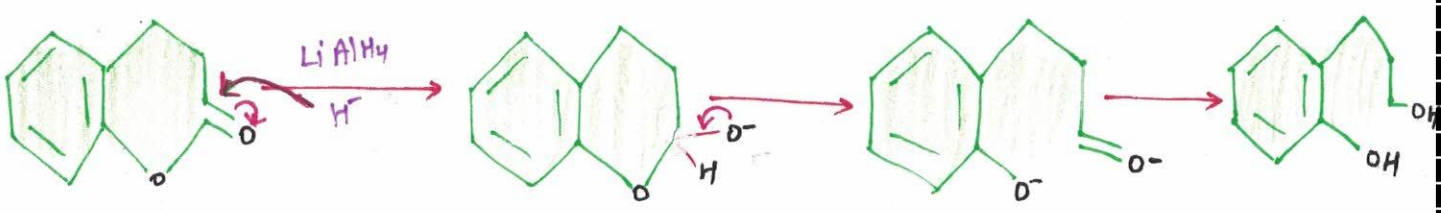


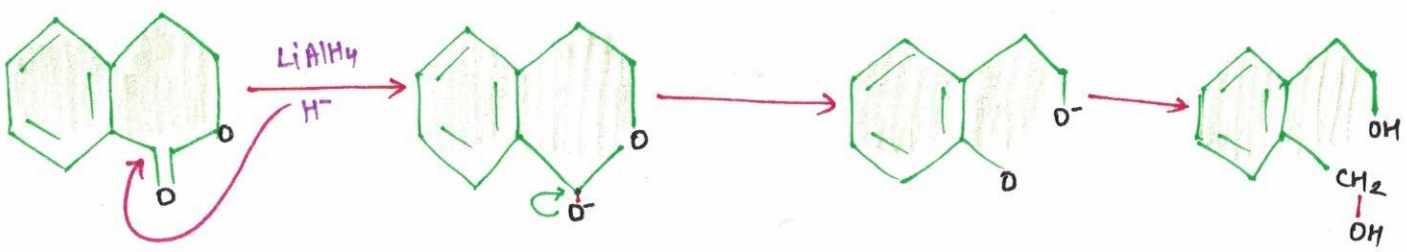




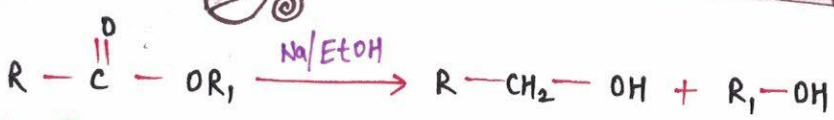
1 ester requires 2 $H^{\ominus}$



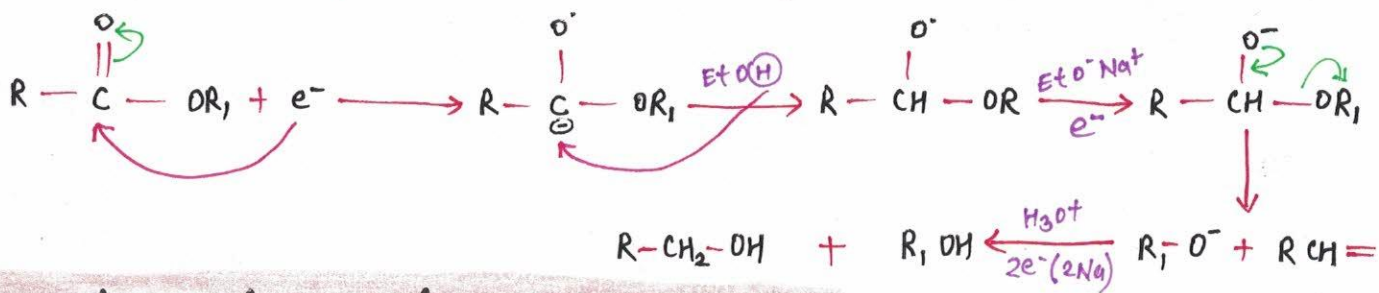




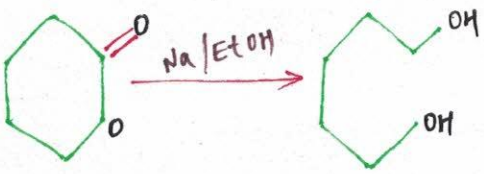
By Bouvault blanc reduction of esters

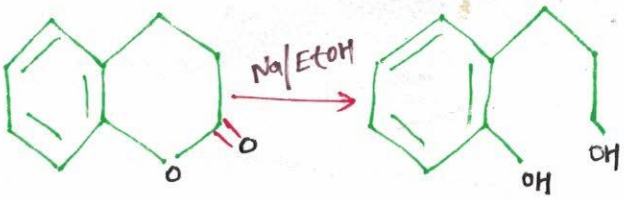


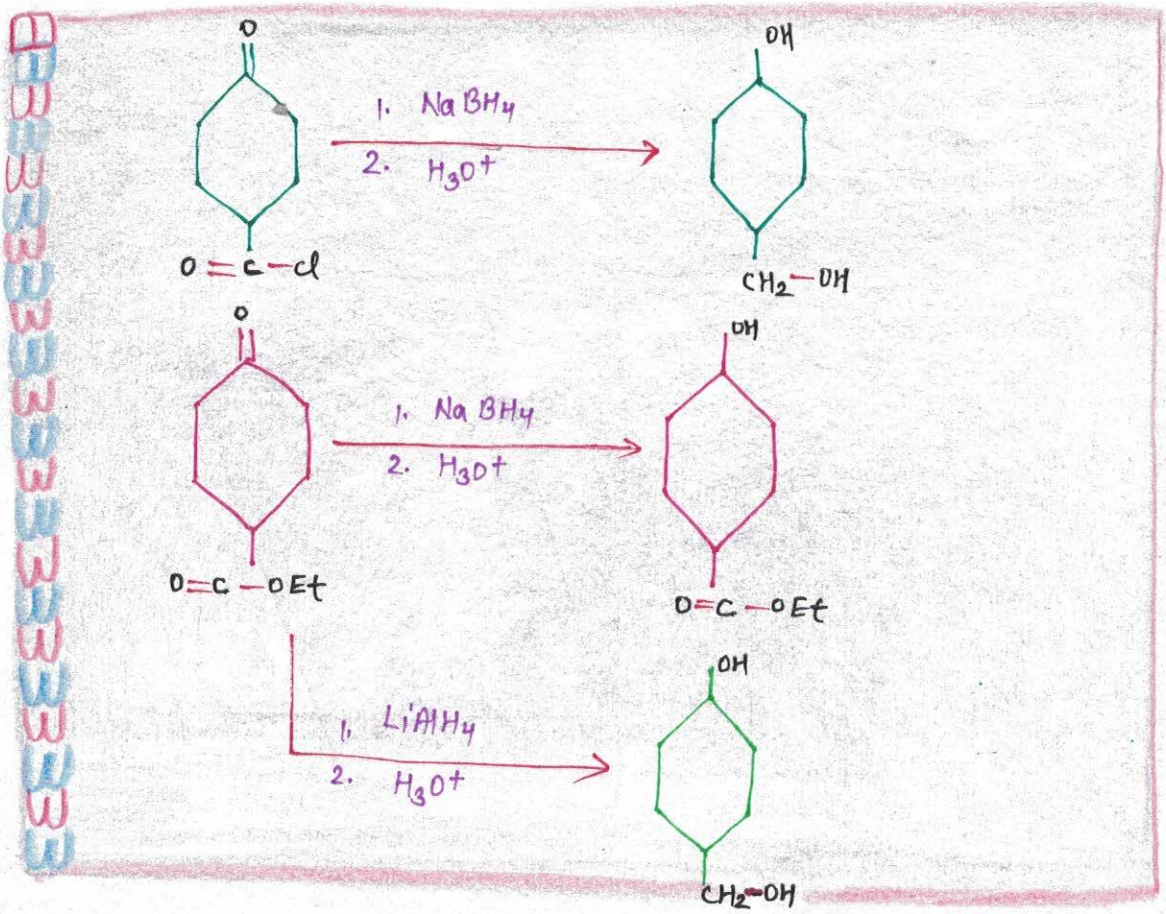
Mechanism



one ester requires 4 mole sodium.

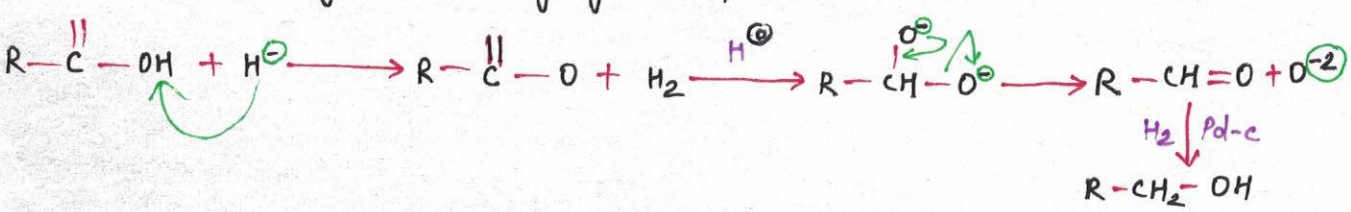






By reduction of carbonylic acids

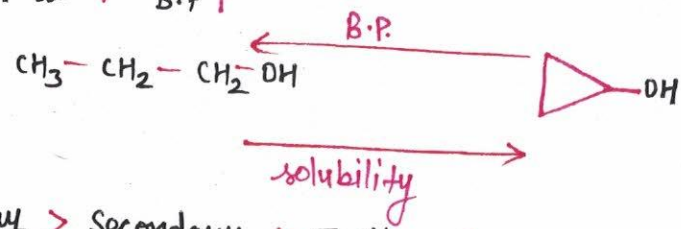
cannot be reduced by $NaBH_4$, only by $LiAlH_4$.



PROPERTIES OF ALCOHOLS

PHYSICAL

Molecular wt. ↑ B.P ↑



{ Primary > Secondary > Tertiary } (Acidic nature)

EtOH < H_2O < EtSH
EtOH < H_2O < PhOH
EtOH < H_2O < HO – CH_2 – CH_2 – OH

} Acidic nature

CHEMICAL PROPERTIES.

They are devided into two groups –

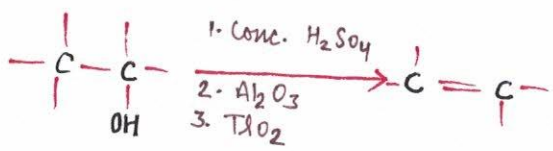
1. Reaction due to C–O bond cleavage.
2. Reaction due to O–H bond cleavage.

when co bond cleavage occurs, the intermediate is R^+ (carbocation). so in such cases rate of reaction ⟶ MeOH < 1° < 2° < 3°

If OH bond cleavage is involved, rate of reaction is proportional to acidic nature of alcohol. In such cases, rate of reaction ⟶ MeOH < 1° < 2° < 3°

Reaction due to C–O bond cleavage

Dehydration of alcohols –



Refer to alkene chapter.

Reaction with HX

$R-OH + PCl_5 \longrightarrow R-Cl + POCl_3$

$R-OH + PCl_5 \longrightarrow R-Cl + H_3PO_3 + HCl$

$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$

{Refer alkyl halide preparation}

$R-OH + \begin{matrix} PCl_5 \\ PCl_3 \\ SOCl_2 \end{matrix} \longrightarrow R-Cl$

$CH_2(OH)-CH_2(OH) + \begin{matrix} PCl_5 \\ PCl_3 \\ SOCl_2 \end{matrix} \longrightarrow CH_2Cl-CH_2Cl$

$R-OH + PBr_3 \longrightarrow R-Br$

$R-OH + P\,I_2 \longrightarrow R-I$

$CH_2(OH)-CH_2(OH) + PBr_3 \longrightarrow CH_2(Br)-CH_2(Br)$

Glyceral $\longrightarrow$ 5 mole HI

Glycol $\longrightarrow$ 3 mole HI

$CH_2(OH)-CH_2(OH) + PI_3 \longrightarrow CH_2(I)-CH_2(I)$

$CH_2=CH_2 \xrightarrow{HI} CH_3-CH_2-I$

$CH_2(OH)-CH(OH)-CH_2(OH) \xrightarrow{3HI} CH_2(I)-CH(I)-CH_2(I) \longrightarrow CH_2=CH-CH_2-I \xrightarrow{HI} CH_3-CH(I)-CH_2-I$

$CH_3-CH(I)-CH_3 \xleftarrow{HI} CH_3-CH=CH_2$

Williamson's etherification

$CH_3-CH_2-OH \xrightarrow[140^\circ C]{\text{conc. } H_2SO_4} CH_3-CH_2-O-CH_2-CH_3$

$CH_3-CH_2-OH \xrightarrow{H^+} CH_3-CH_2-OH_2 \longrightarrow CH_3-CH_2^{\oplus} \xrightarrow{:O(-CH_2-CH_3)_2} CH_3-CH_2-O^{\oplus}(H)-CH_2-CH_3 \xrightarrow{-H^+} CH_3CH_2-O-CH_2CH_3$

With conc H_2SO_4 at Low temp. $\longrightarrow$ elimination

With conc H_2SO_4 at high temp. $\longrightarrow$ substitution

$CH_3-CH_2-OH + \text{conc. } H_2SO_4 \text{ (cold)} \longrightarrow CH_3-CH_2-O-S(=O)_2-OH$

Reactions due to O-H bond cleavage

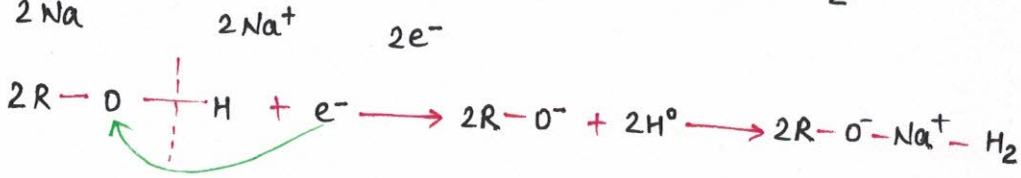
1. With Na metal

$$2R-OH + 2Na \longrightarrow 2R-O^-Na^+ + H_2\uparrow$$

It is a test to identify alcohols.

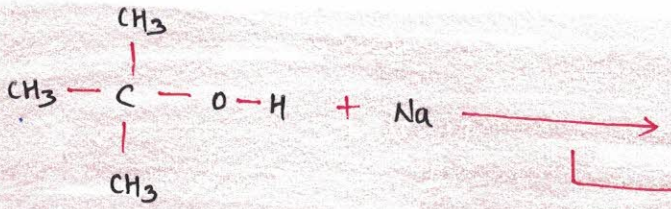
Alcohol react with Na & liberate H_2.

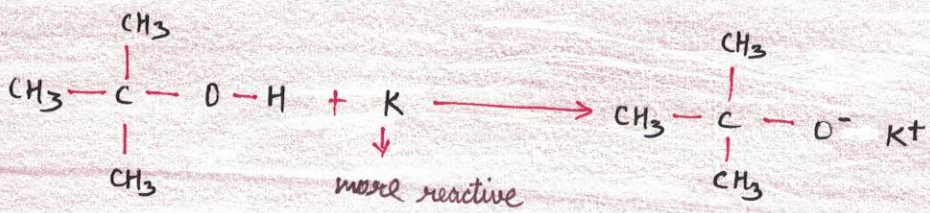
Mechanism –



Rate of Reaction – $CH_3-O-H > 1 > 2 > 3$

Rate of Reactivity – Cs > Rb > K > Na > Li





Any compound having acidic hydrogen react with Na to liberate H_2.

Williamson's Synthesis

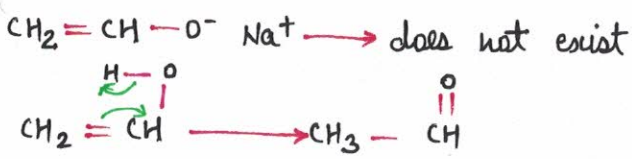
$$R-O-H \xrightarrow{Na} R-O^-\ Na^+ \xrightarrow{R-CH_2X} R-O-CH_2-R \text{ (ether)}$$

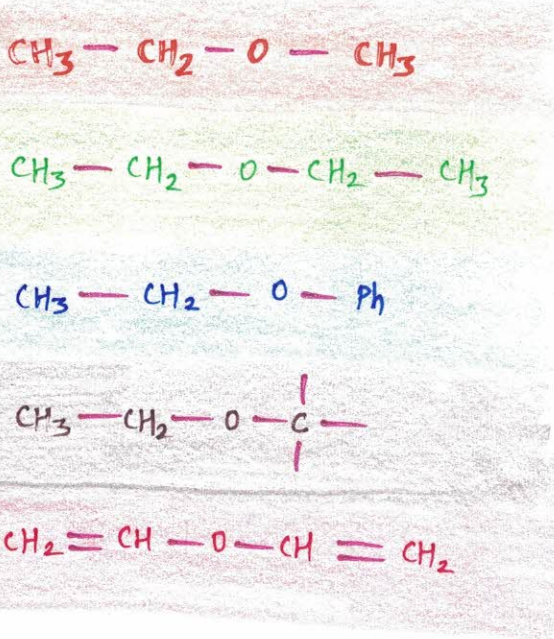
$CH_3-O-CH_2-CH_3$ — Preparation

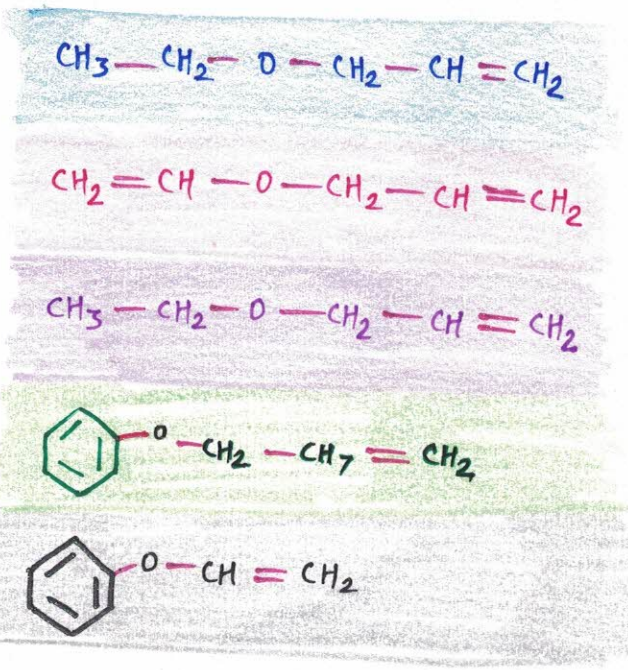
$$CH_3CH_2OH \xrightarrow{Na} CH_3CH_2O^-\ Na^+ \xrightarrow{CH_3-X} CH_3-CH_2-O-CH_3$$

$$CH_3OH \xrightarrow{Na} CH_3O^-\ Na^+ \xrightarrow{CH_3CH_2X} CH_3CH_2OCH_3$$

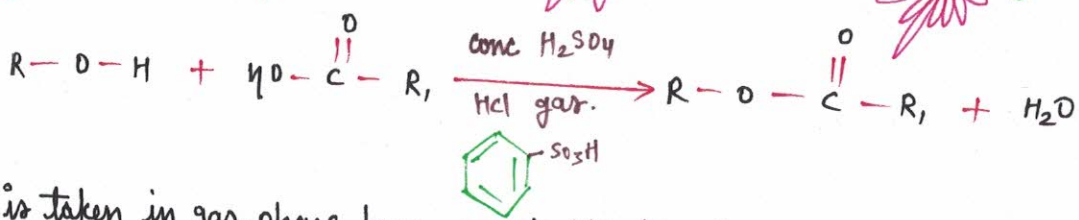
$CH_2=CH-O-CH_2-CH=CH_2$ → cannot be prepared.

because  does not exist



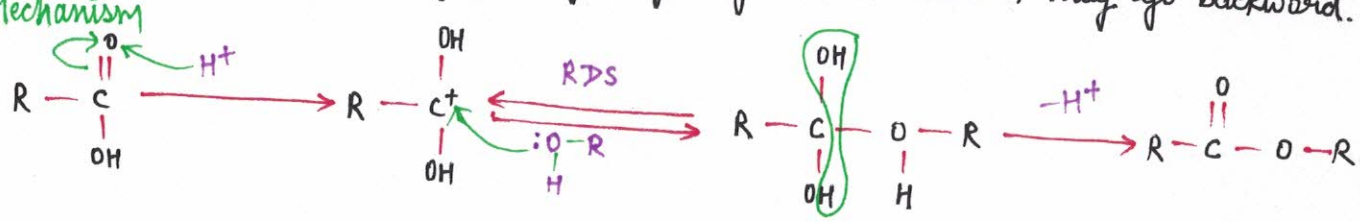


Williamson's Esterification

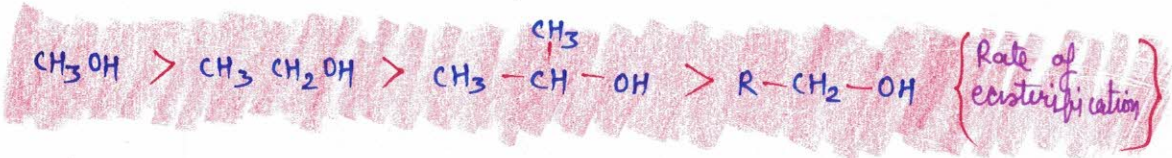


HCl is taken in gas phase because esterification is reversible & if H_2O is present in liq. form ester formed may undergo hydrolysis and reaction may go backward.

Mechanism



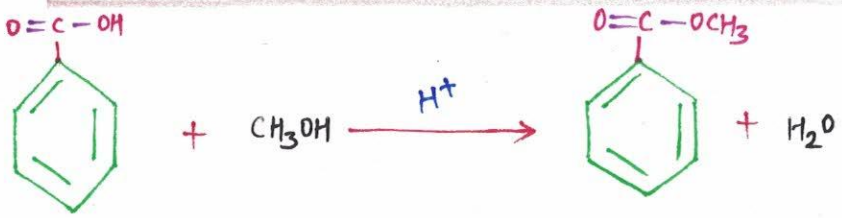
As crowding affects nucleophilicity,

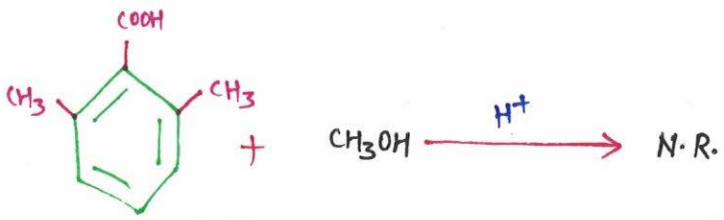


As it is OH bond cleavage, rate also depends on the acidic nature of alcohol. Similarly as crowding in acid reactivity decreases. so most reactive acid is {Formic acid}

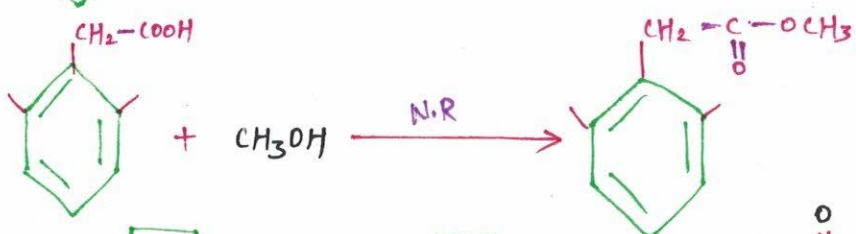
$HCOOH > CH_3COOH > CH_3CH_2COOH > CH_3-\underset{CH_3}{\underset{|}{CH}}-COOH > CH_2\left(\underset{CH_3}{\underset{|}{C}}-CH_2COOH\right)_{CH_3}$

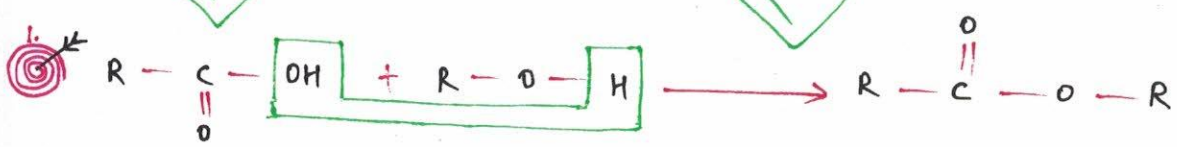
$CH_3OH + HCOOH \longrightarrow$ Most reactive mixture

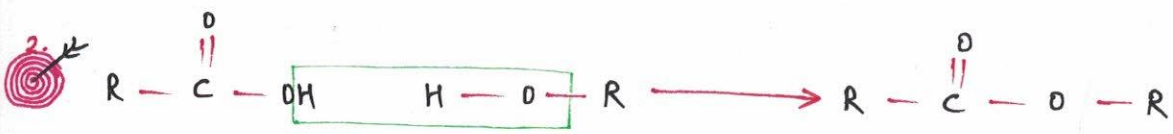




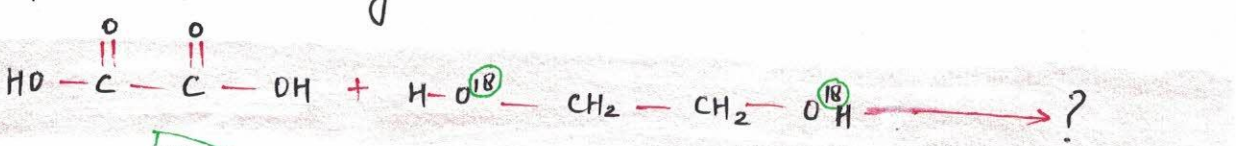
It does not react even on refleasing (boiling).

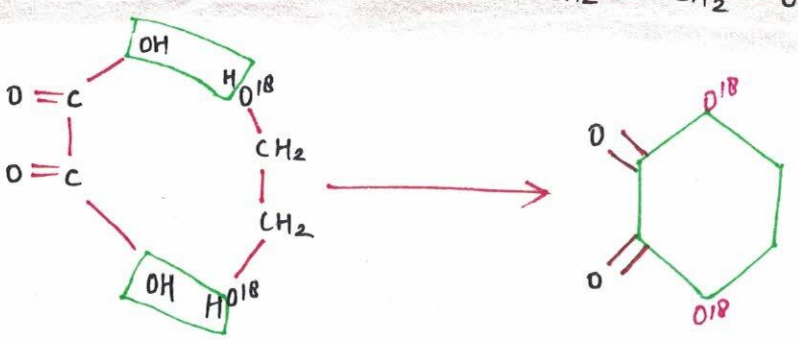


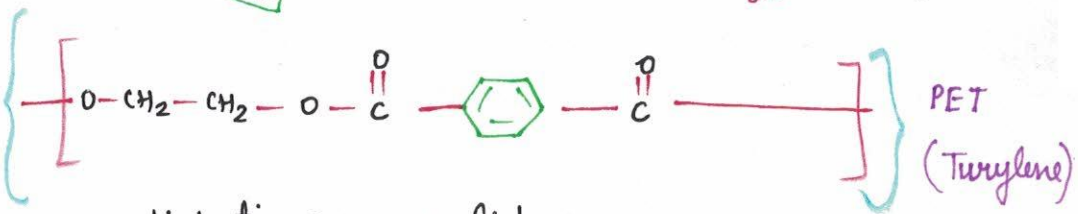




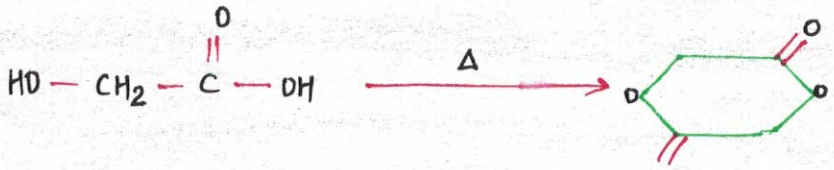
(1.) occurs but (2.) does not because if co bond cleavage occurs as in (2.) then 3° 2° 1° ME but 3° does not even undergo hydrolysis do we proove that only (1.) occurs. Experimentally, if we put a labelled O^{18} in alcohal then in ester O^{18} was found which process above theory.



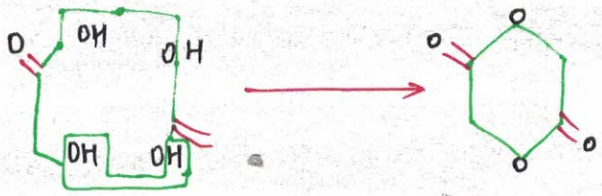


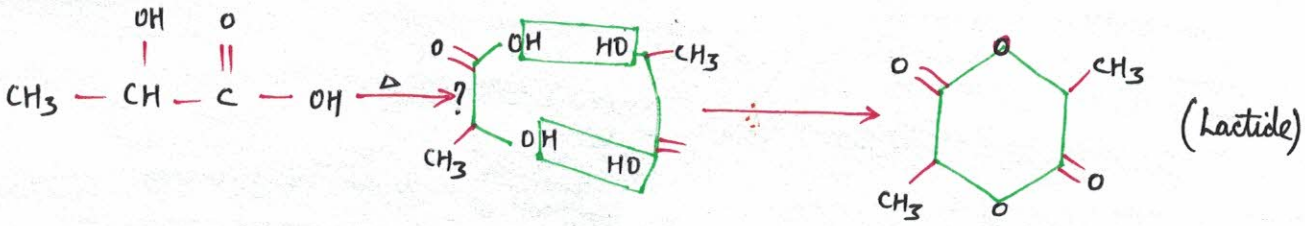


No continuous C–C linkage.

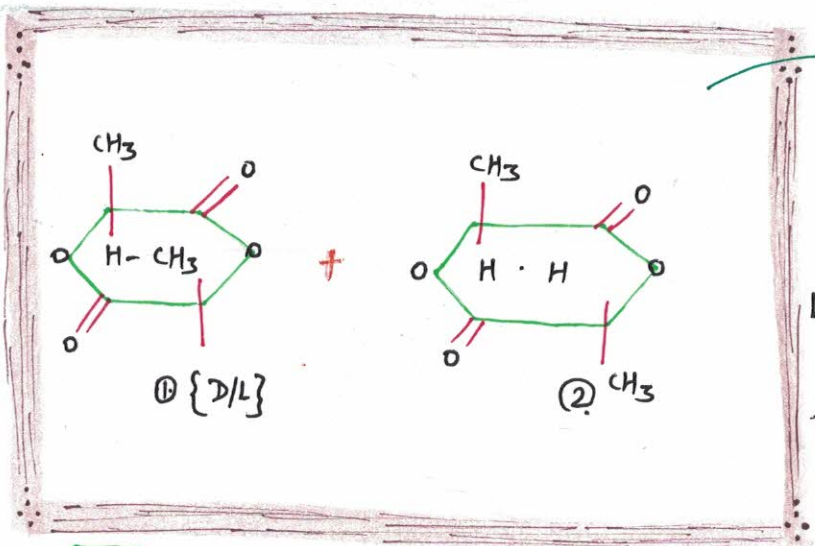


(Lactide)





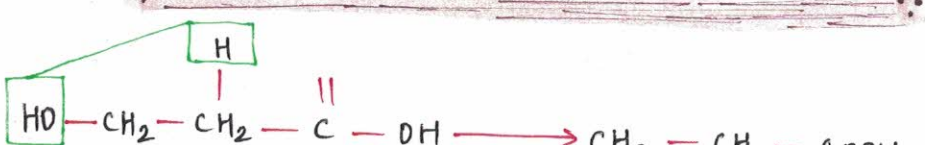
(Lactide)



① {D/L}

② CH_3

Take mirror Image and then rotate to superimpose it.
② has a centre of symmetry. Groups on diagonals are same. Hence it is inactive.
But ① is optically active as its mirror image do not superimpose.
So Total ③ isomers are formed.



(crotonic acid)

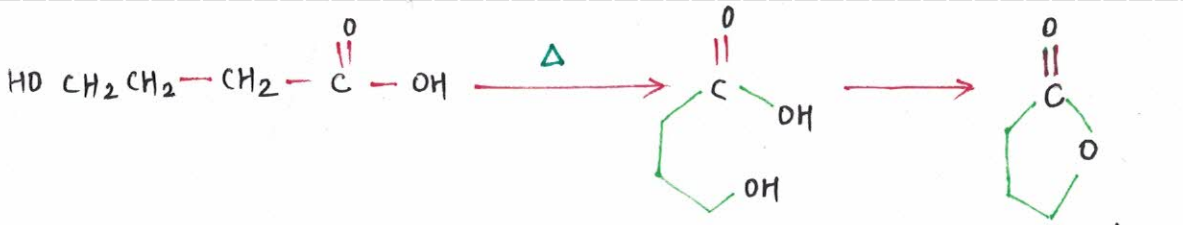
α hydroxy $\xrightarrow{\Delta}$ Lactides (cluster)

β hydroxy $\xrightarrow{\Delta}$ 1,2 unsaturated acid

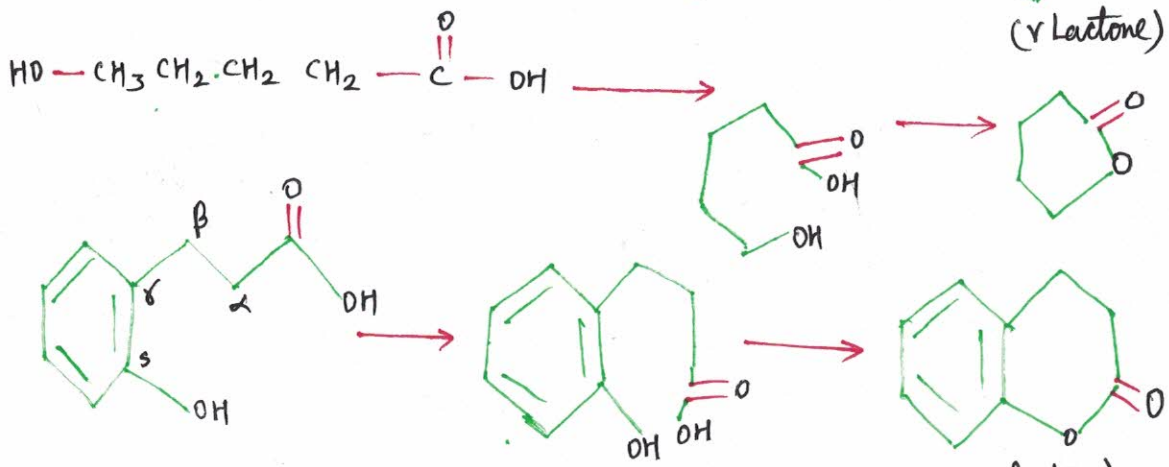
γ, δ hydroxy → γ lactone { Lactone }

ω hydroxy → macro molecule (Polymer)

only β hydroxy does not give ester.



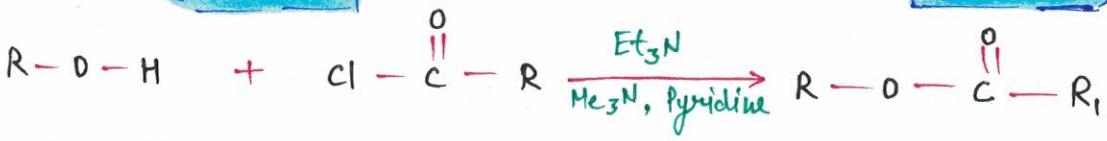
(γ Lactone)



(δ lactone)

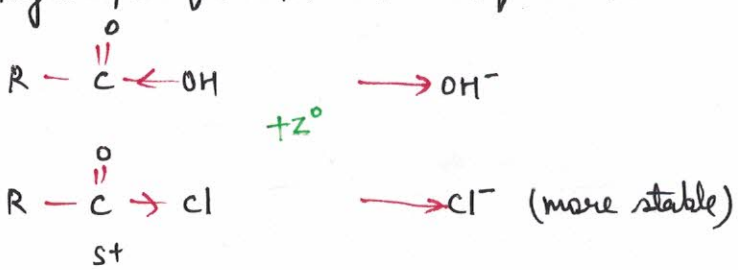
With higher than 6 carbons, esters are not formed due to unstable rings, In these cases, mostly polymers are formed.

Acylation of Alcohols

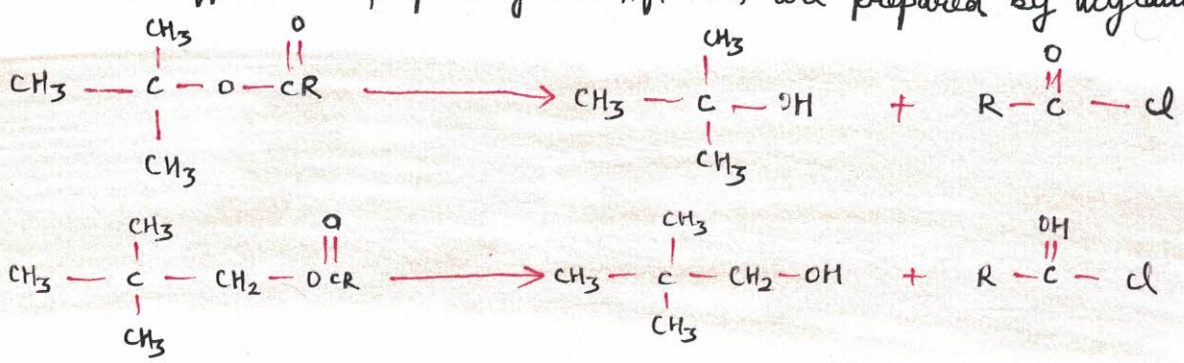


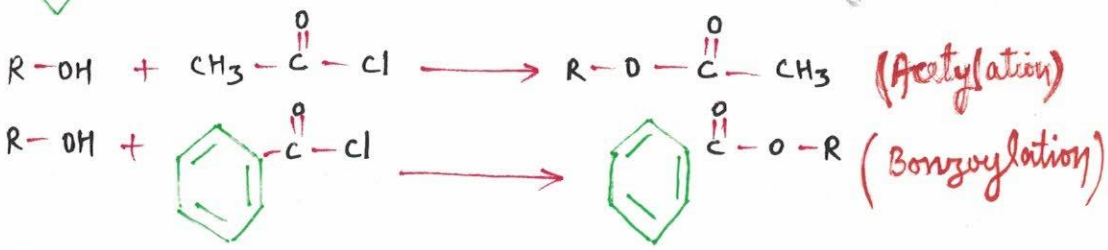
In esterification, leaving group is OH^- but in acylation leaving group is acid chloride ion which is more stable.

Acylation is faster than esterification.



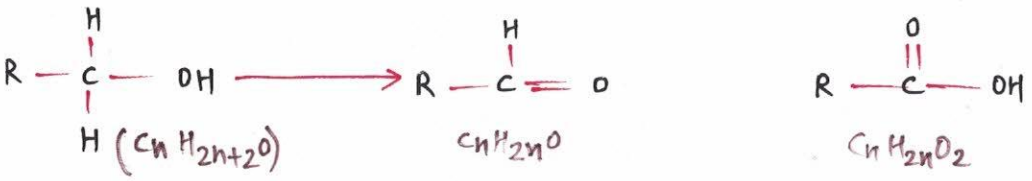
Esters which are difficult to prepare by esterification are prepared by acylation.



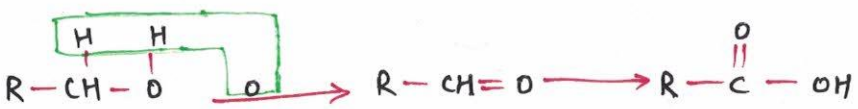


It can be also done by $(Ac)_2O$.

OXIDATION

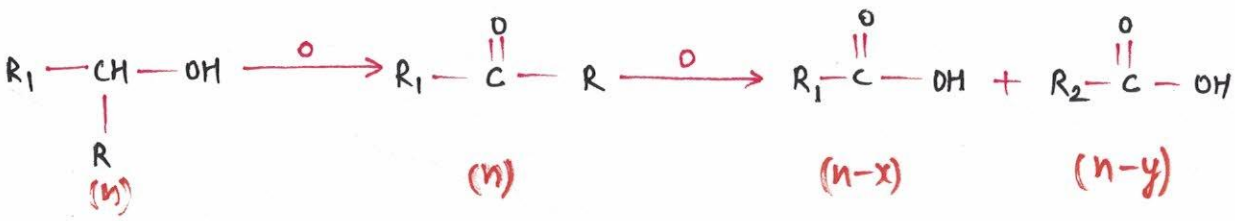


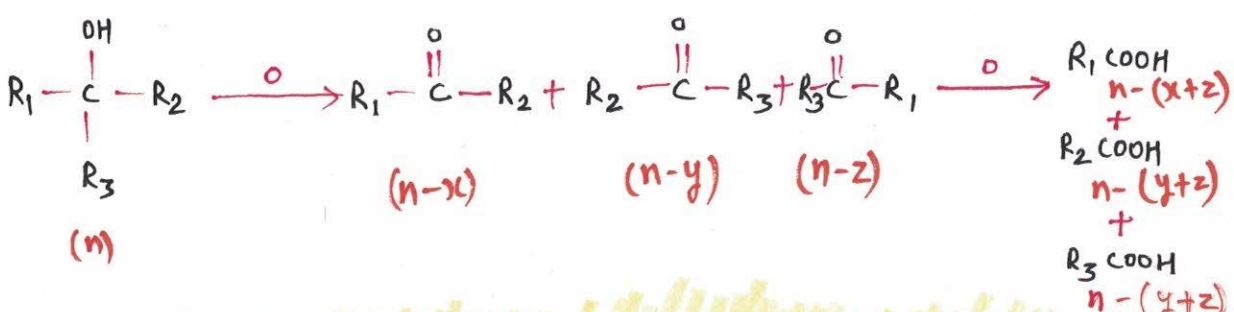
MECHANISM



If no. of c in alcohol and no. of c in acid are same on oxidation, then the alcohol must be primary.

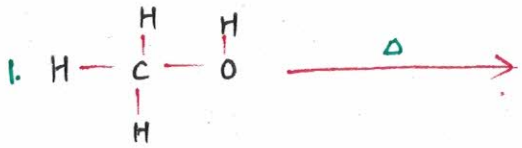
If we get less no. of c then alcohol is not primary.

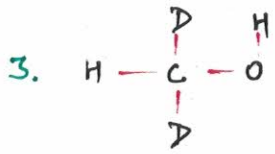


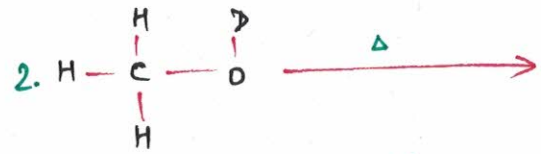


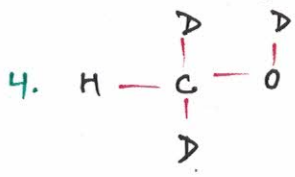
Oxidation of oxidation will show hydrogen isotopic effect.

Oxidation of alcohols do not show hydroxy hydrogen isotopic effect.

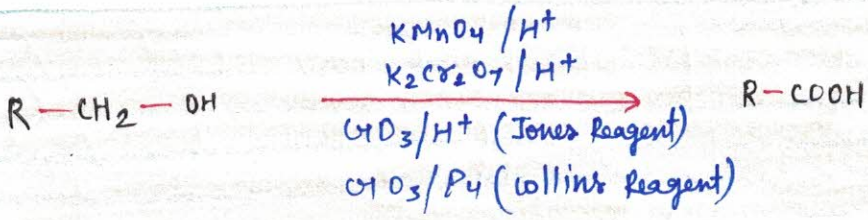


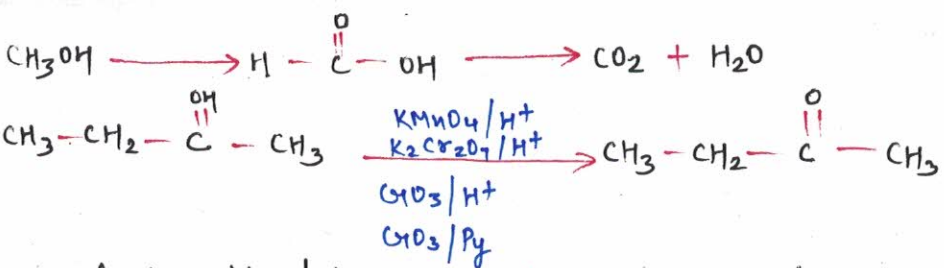




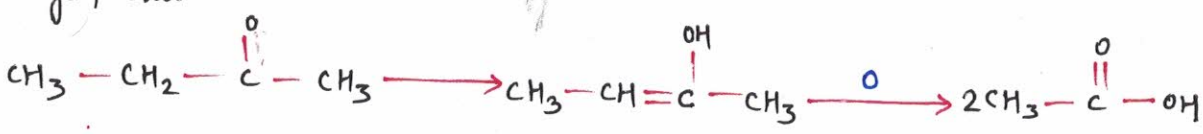


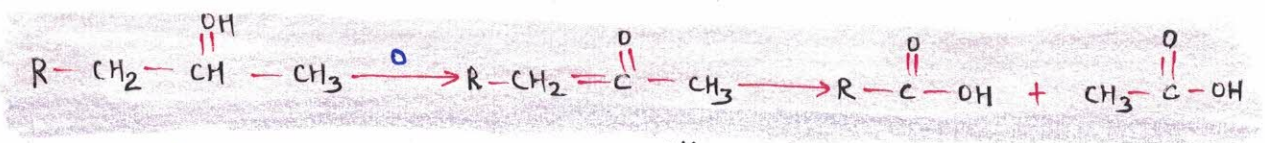
Rate : 1=2 > 3=4 < $CH_3OH > R-CH_2OH > R-\underset{R}{CH}-OH > R-\underset{R}{\overset{R}{C}}-OH$ } oxidation rate

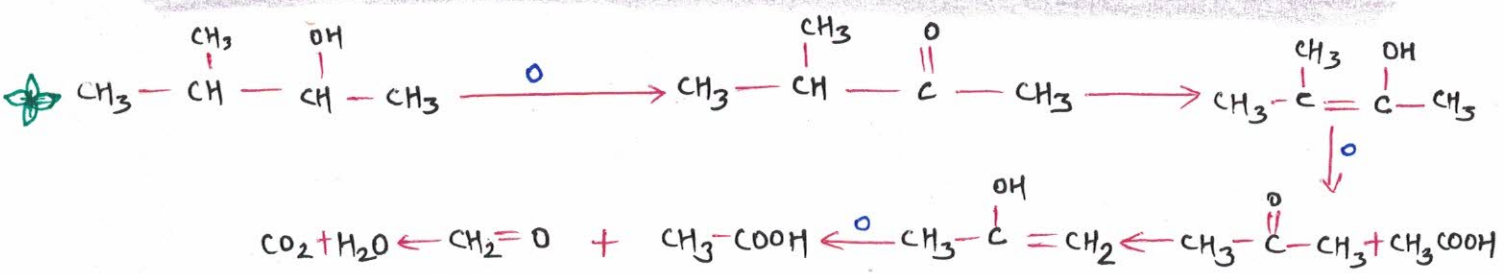


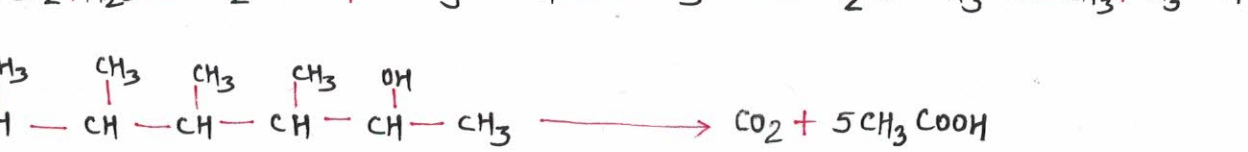


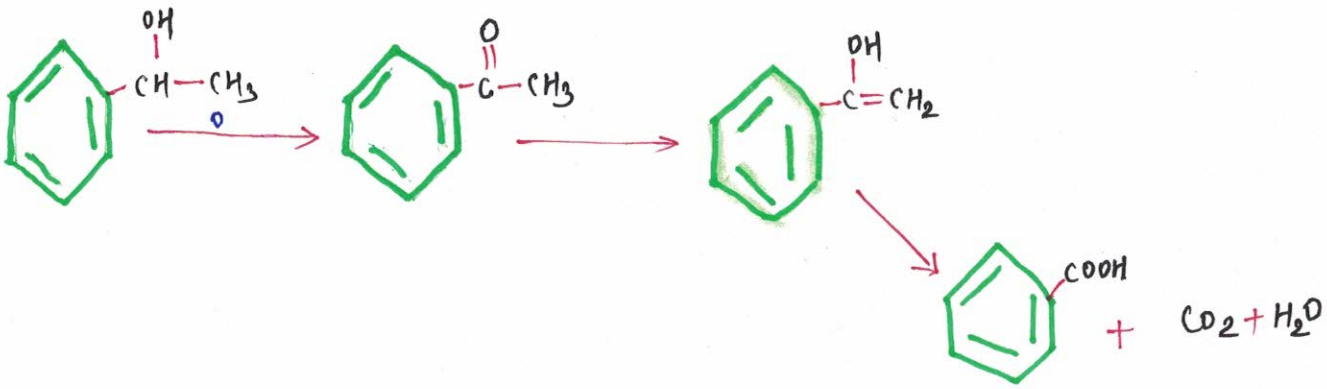
Ketons can only be oxidised by $KMnO_4/H^+$ and when it oxidises it changes to more major enol.

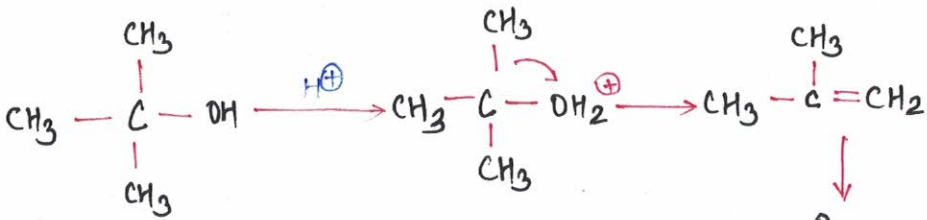


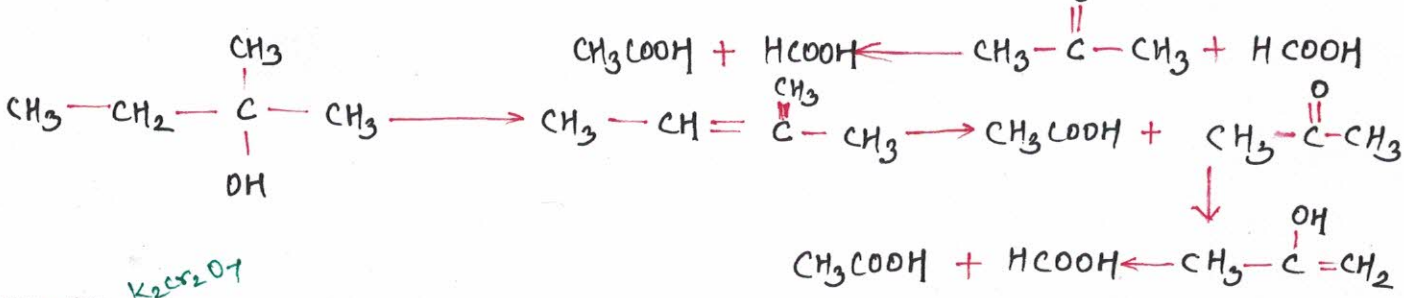


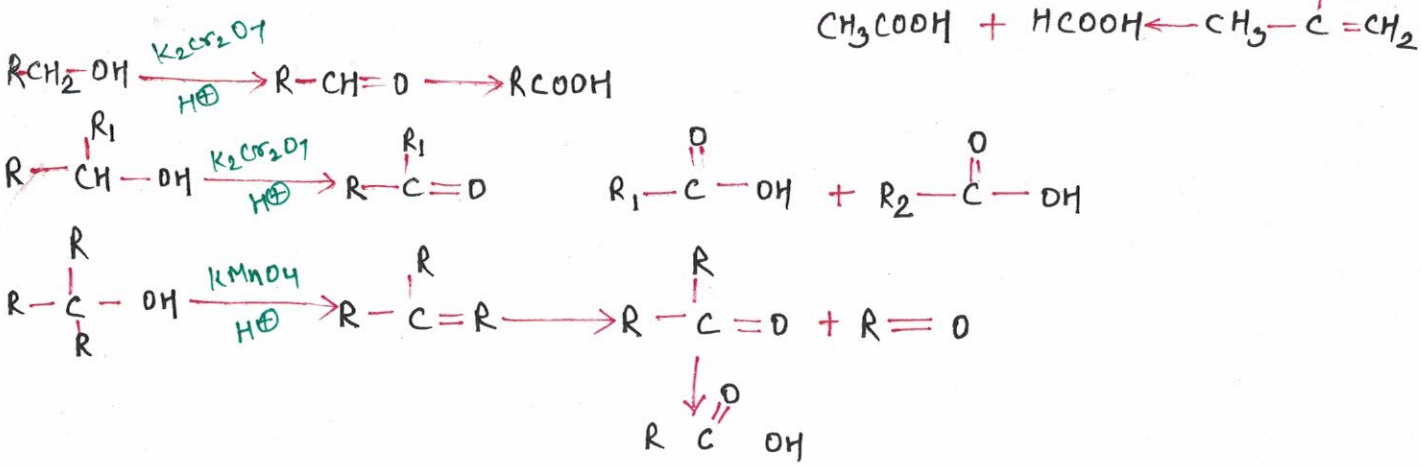




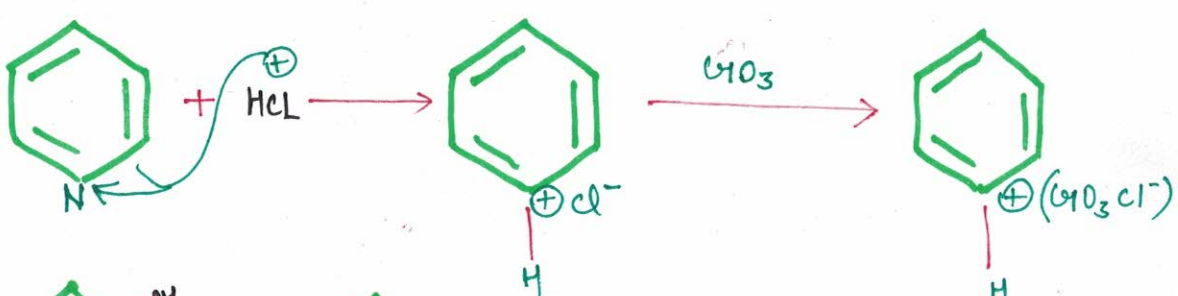


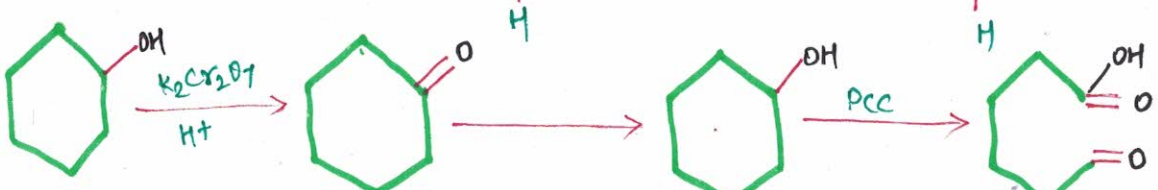


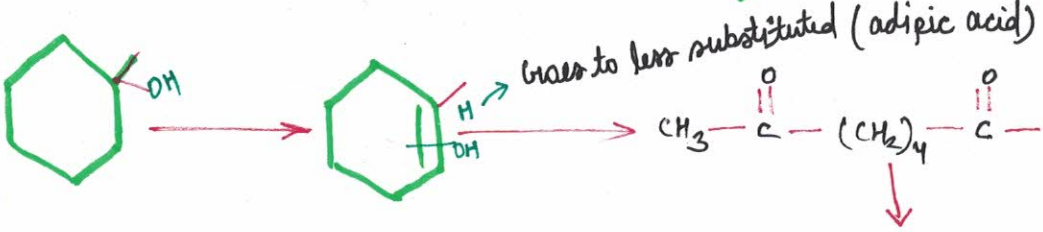




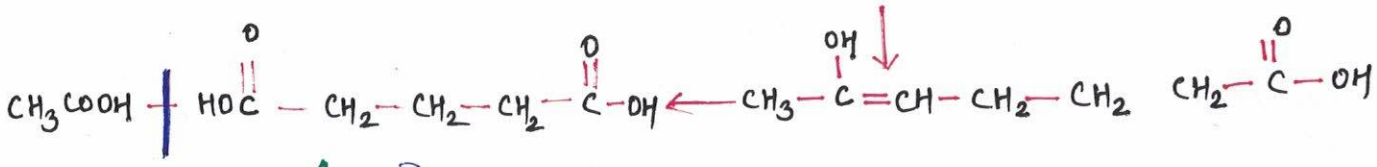
or $R-CH=O$ to not change into RCOOH we use PCC (Pyridinium chlow chromate)



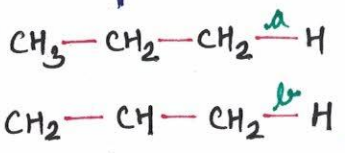




goes to less substituted (adipic acid)



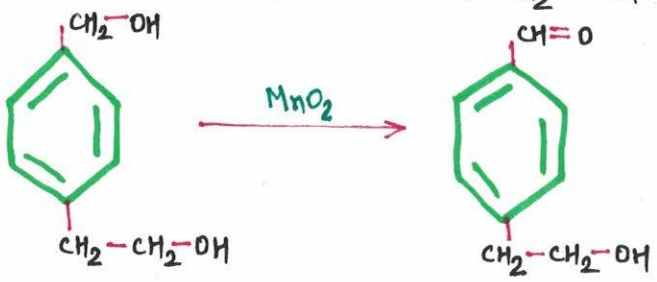
#3



"b" bond is longer & weaker

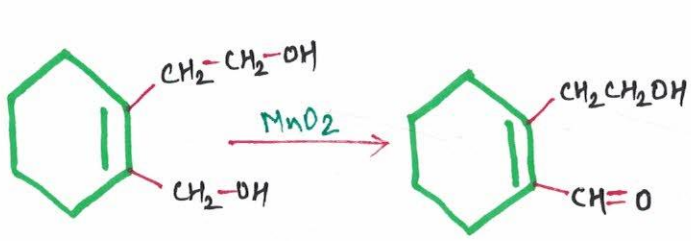
And as oxidation shows α hydrogen isotopic effect to will undergo oxidation more faster than >a' & even undergoes it by MnO_2.

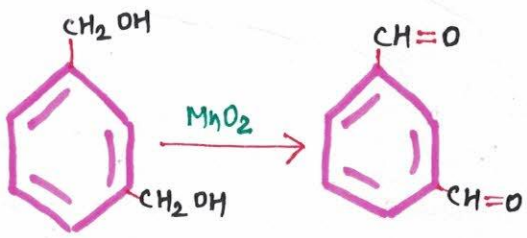
(Akylyde)

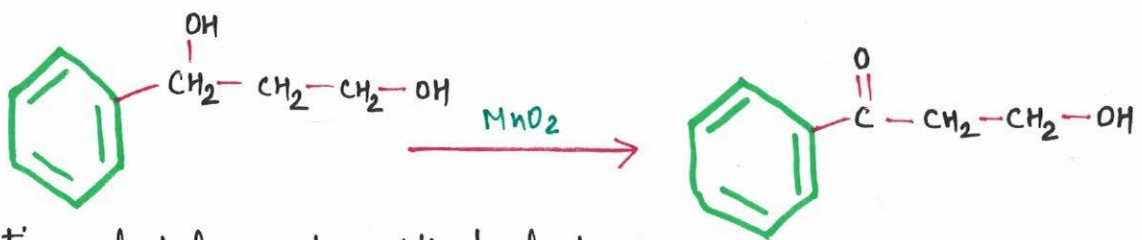


(only allylic alcohols can be oxidised by MnO_2)

or benzylic



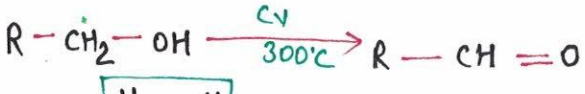


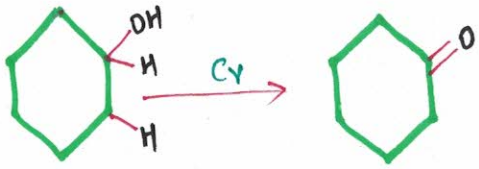


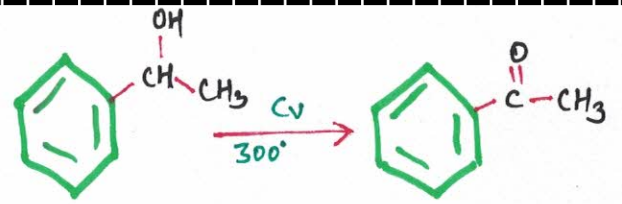
Tertiary alcohols can be oxidised only by $KMnO_4$.

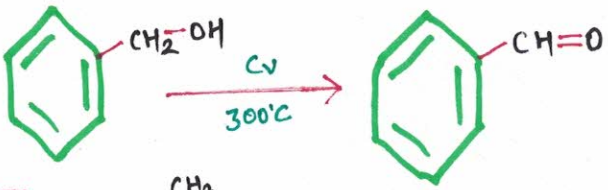
Ketones alcohols can be oxidised only by $KMnO_4$.

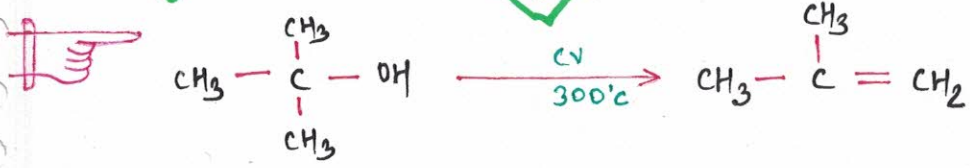
DEHYDRATION OF ALCOHOLS

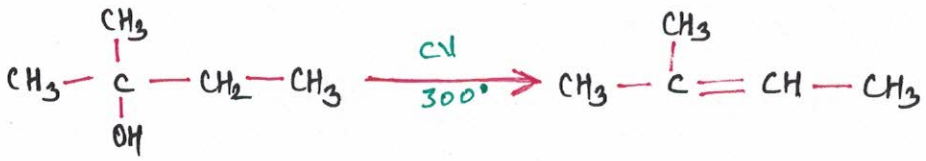






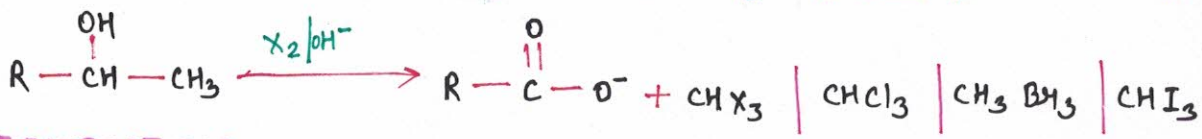






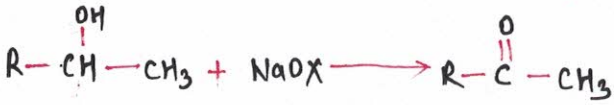
Tertiary alcohol ⟶ Alkene
Secondary alcohol ⟶ ketone
Primary alcohol ⟶ Aldehyde

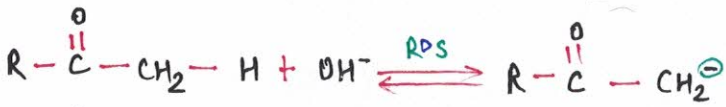
HALOFORM REACTION

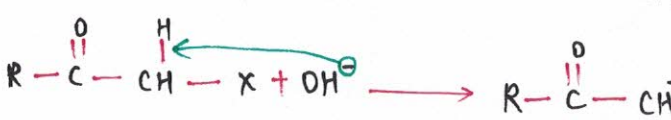


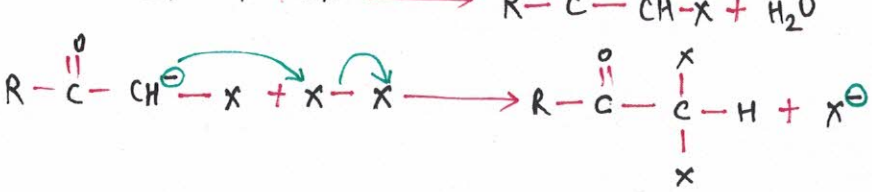
MECHANISM

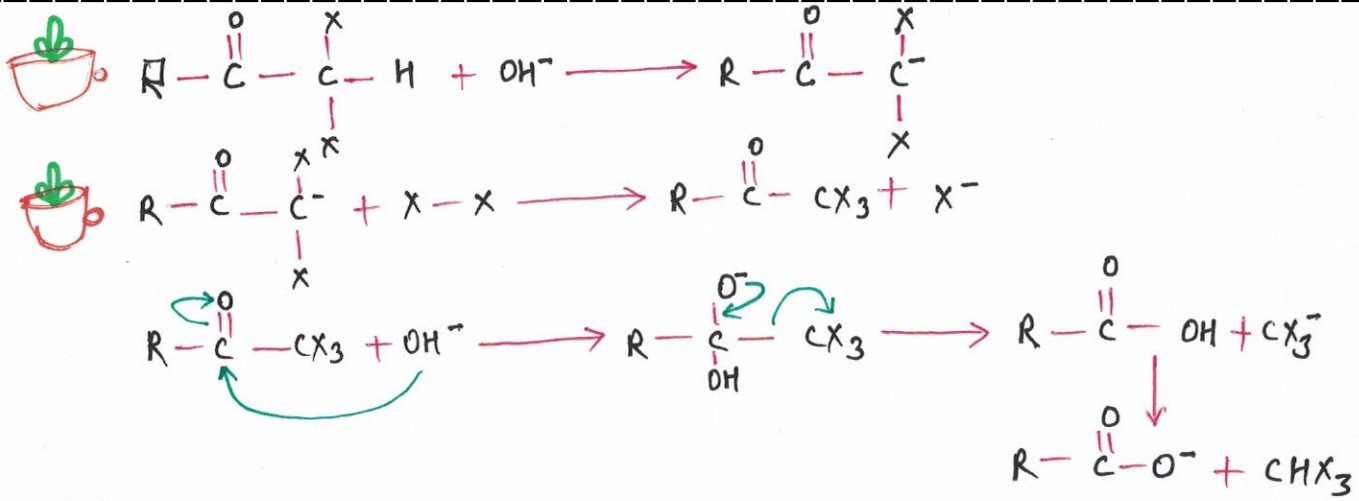
1. $X_2 + NaOH \longrightarrow NaX + NaOX$



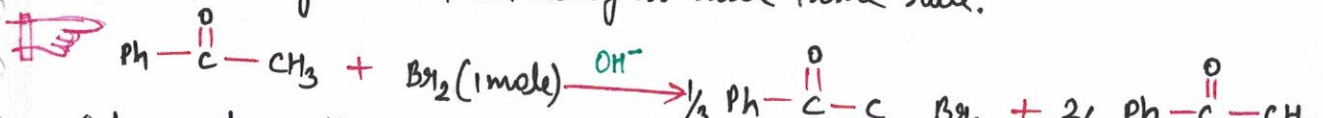








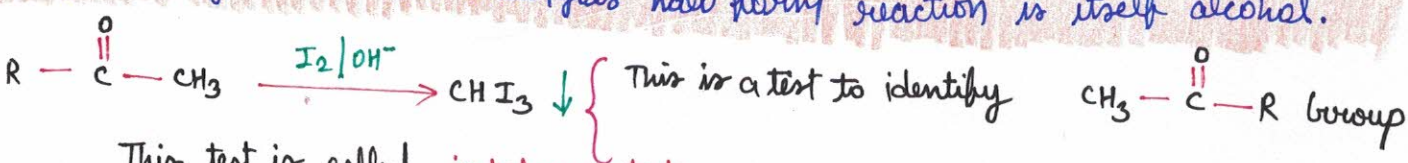
Halo form reactions are "zero order" reaction w.r.t halogens because rate does not depend on halogens and all halogens have same rate.



Subsequent reactions are faster hence mono halogenation is not possible.

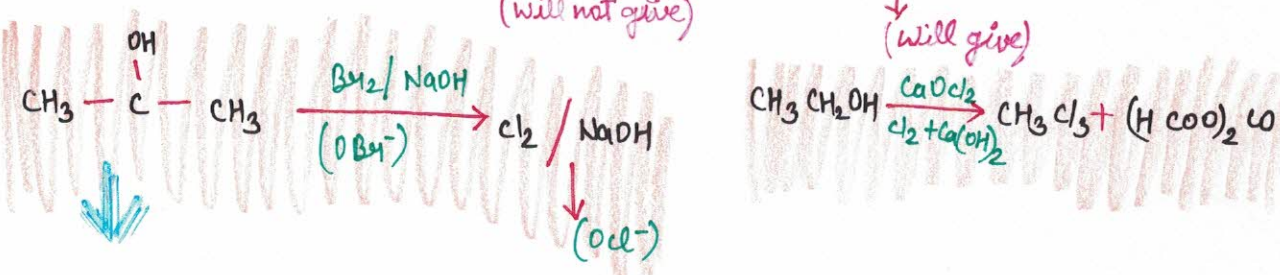
$CHCl_3$ → gas, $CHBr_3$ → liquid, CHI_3 → yellow solid

Only primary alcohol that undergoes halo form reaction is itself alcohol.



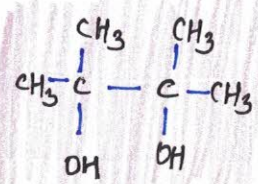
This test is called iodoform test.

Tertiary alcohol does not undergo halo form reaction. Hence it will not give iodoform test to distinguish, $CH_3CH_2\overset{OH}{C}H-CH_2-CH_3$ & $CH_3CH_2CH_2-\overset{OH}{C}H-CH_3$ nee use iodoform test.

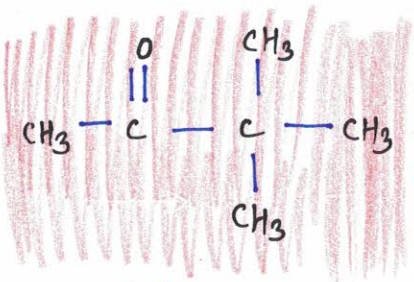


PINACOL - PINACALONE REARRANGEMENT

PINACOL → 2,3 dimethyl 2,3 butanediol

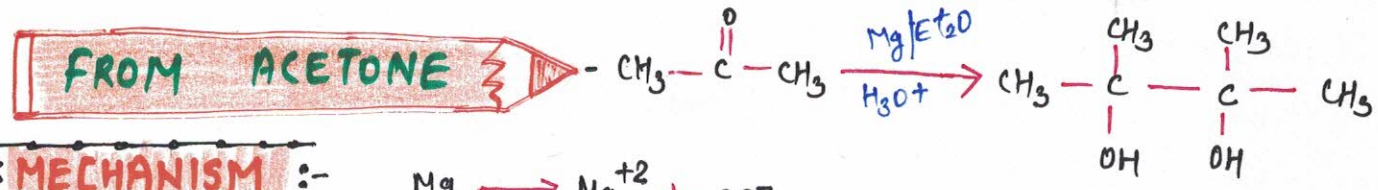


PINACALONS → 3,3 dimethyl 2 butanone

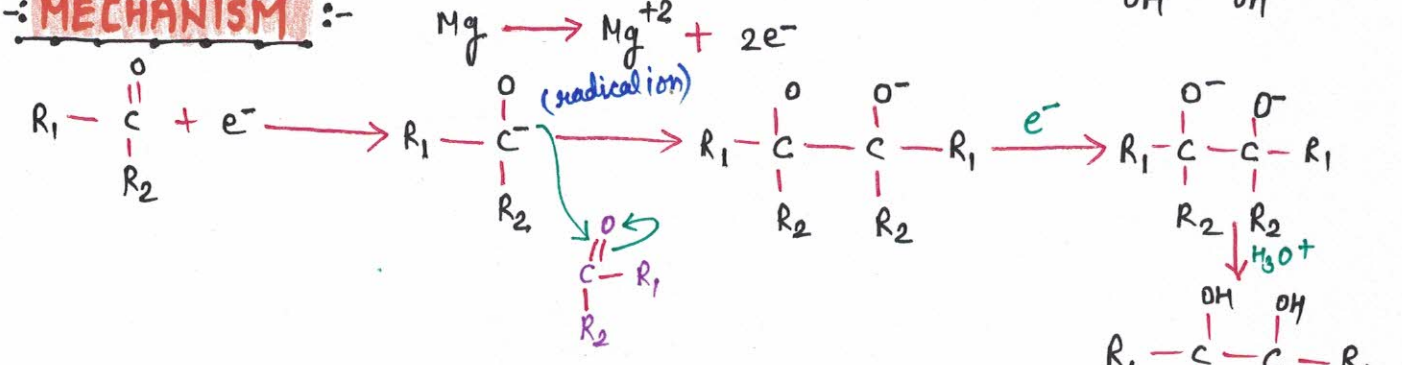


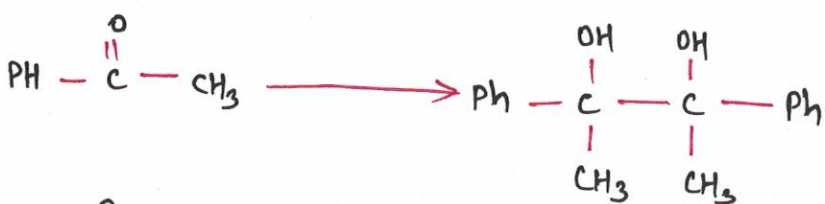
PREPARATION

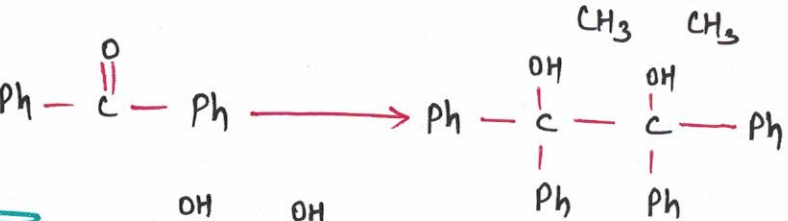
FROM ACETONE

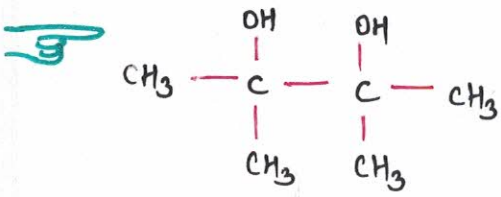


:- MECHANISM :-

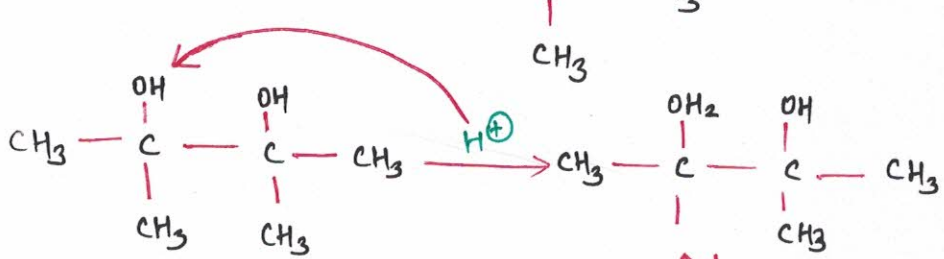


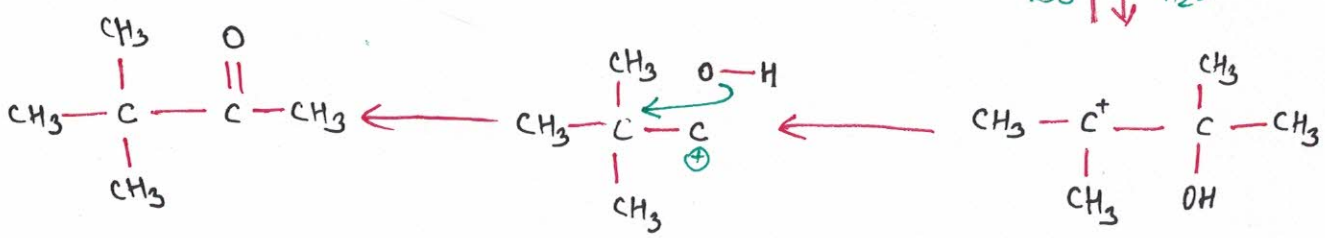


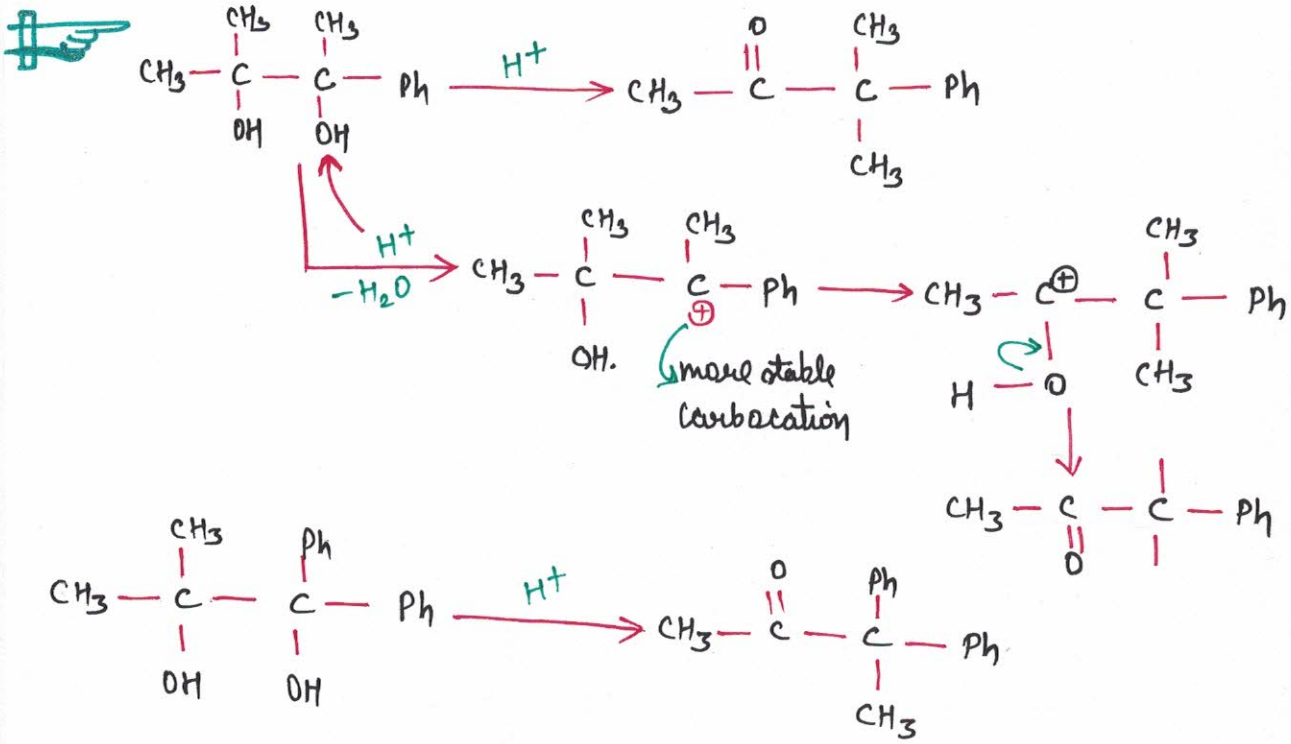


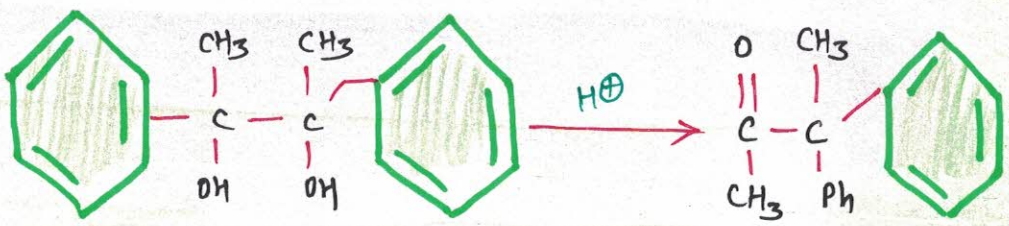


:- MECHANISM :-

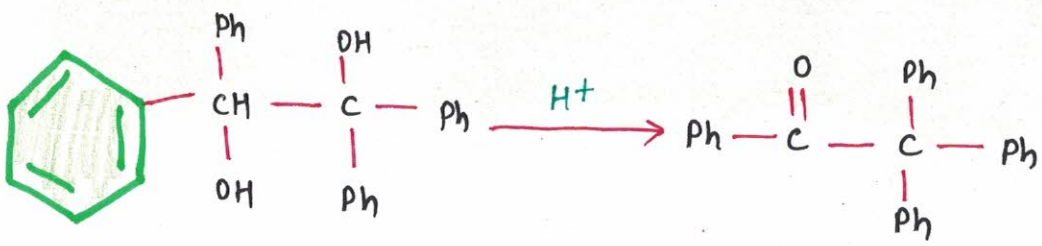


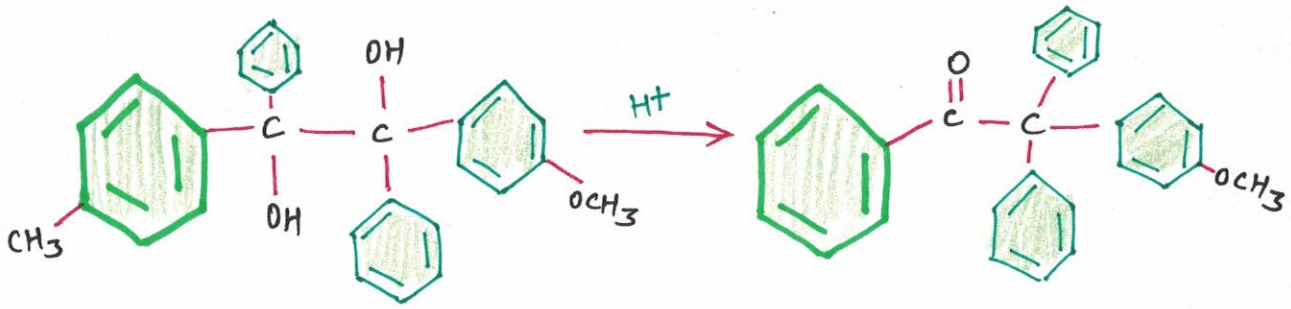


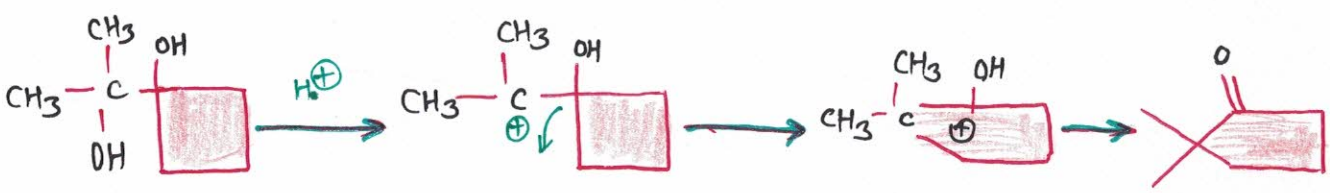


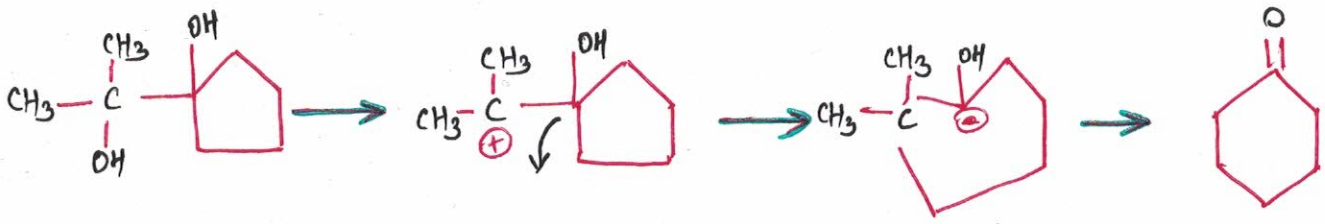


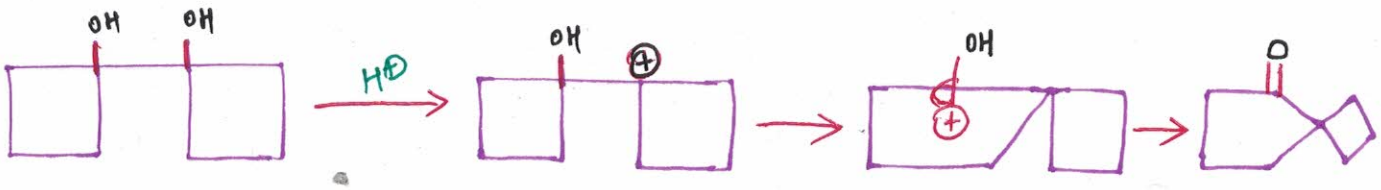
Phenyl shift is faster than methyl shift

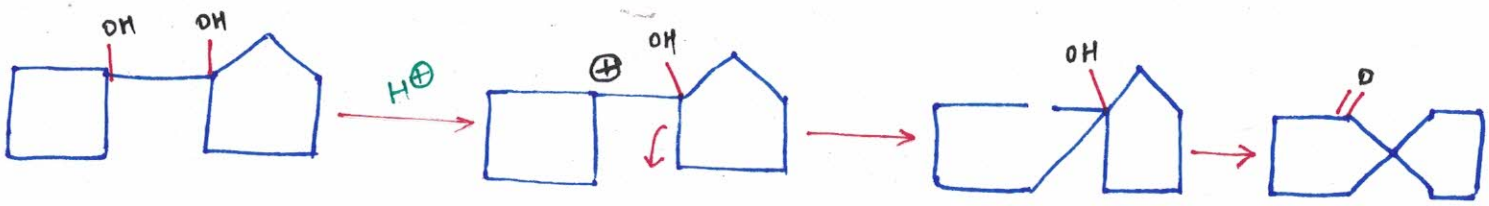


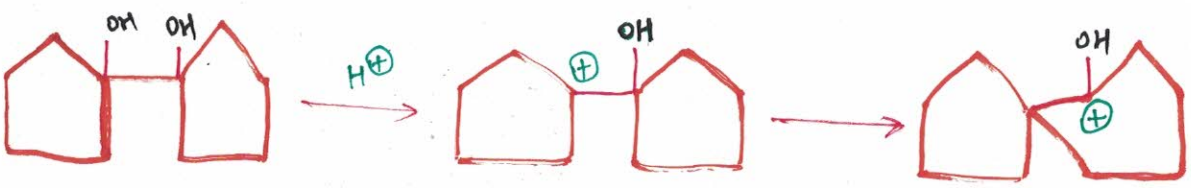


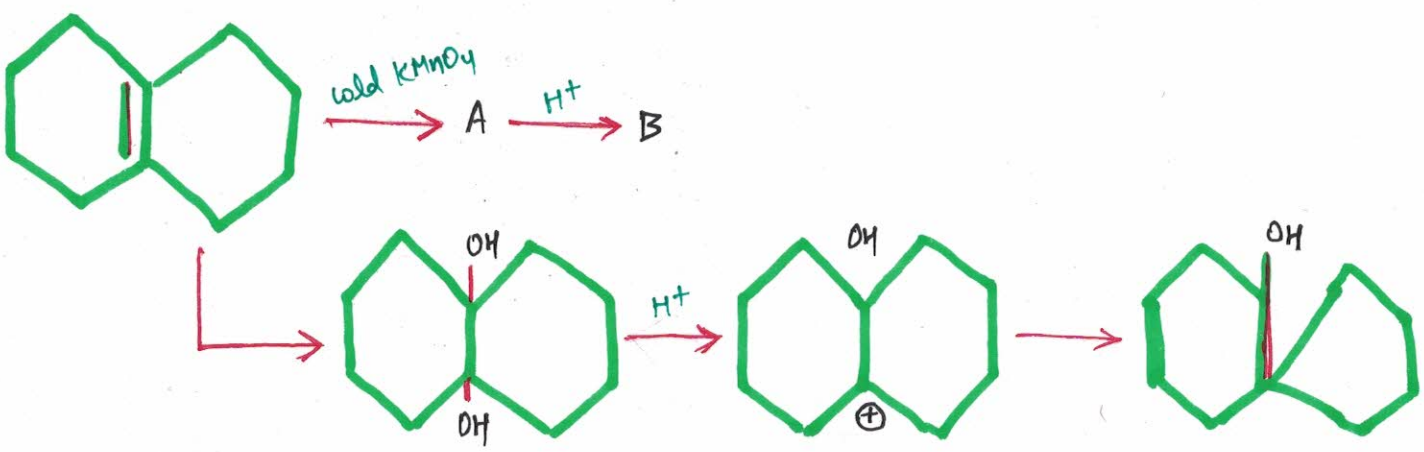


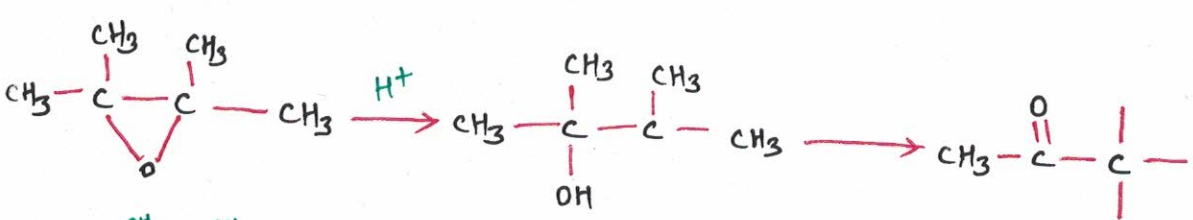


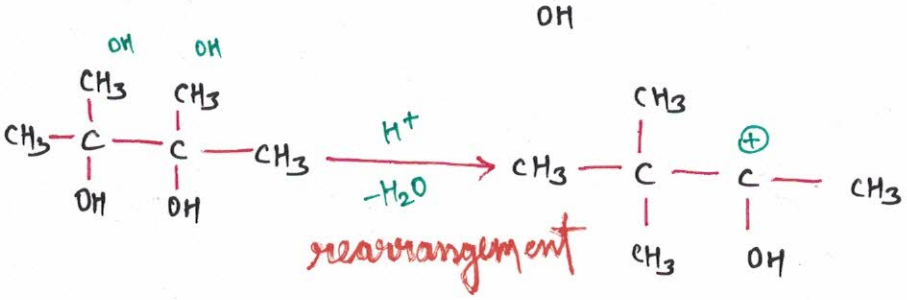


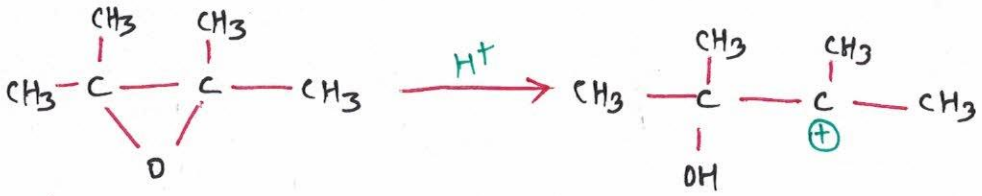


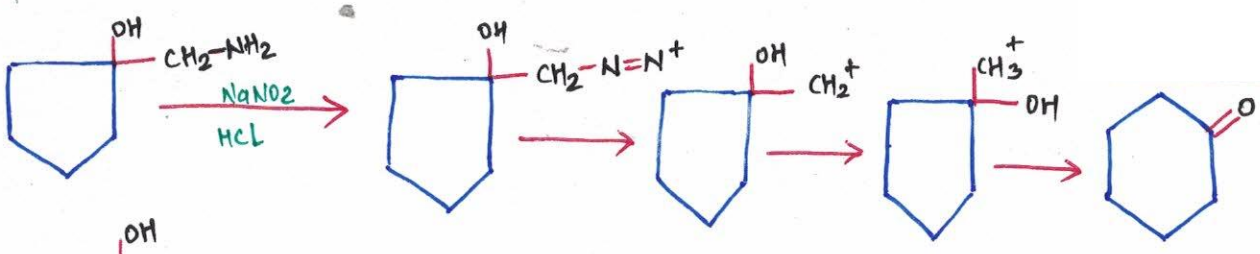


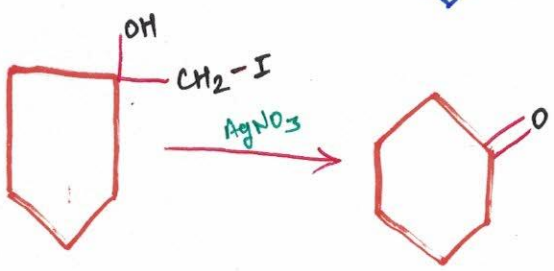


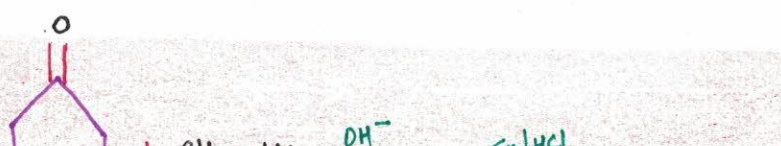


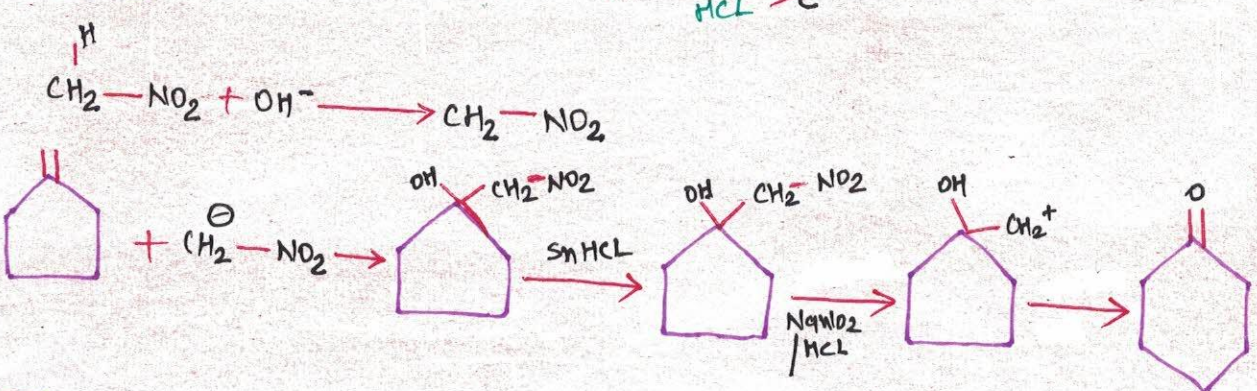




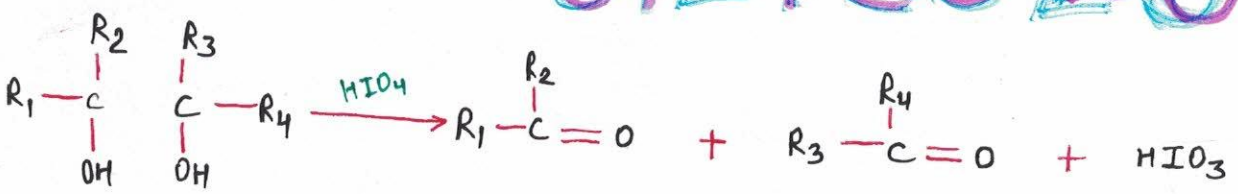




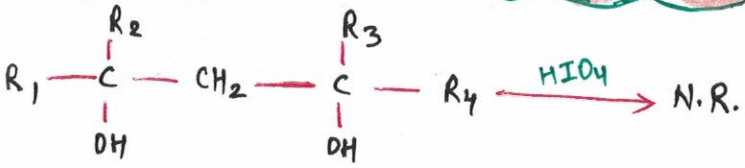




OXIDATION CLEAVAGE OF GLYCOLS



Only 1,2 glycols undergo this reaction



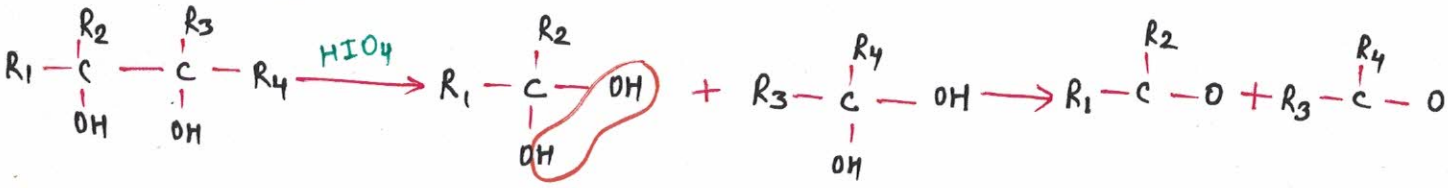
$AgNO_3 + HIO_4 \longrightarrow$ N.R because $AgIO_4$ is soluble

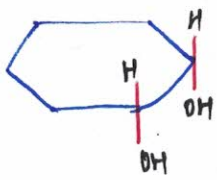
This is a test to distinguish b/w 1,2 glycols & other glycols.

$AgF, AgNO_3, AgClO_4, AgIO_4$ ↓ Soluble

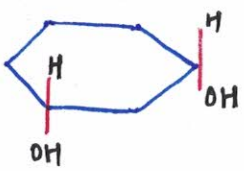
$AgNO_3 + HIO_3 \longrightarrow AgIO_3 + HNO_3$ (yellow ppt.)

:- MECHANISM :-

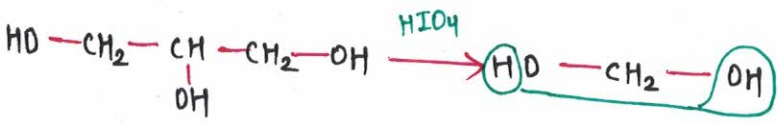


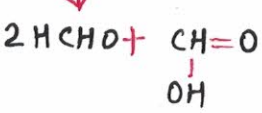


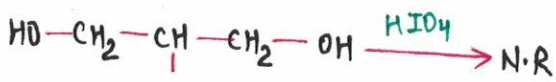
will give oxidative cleavage but

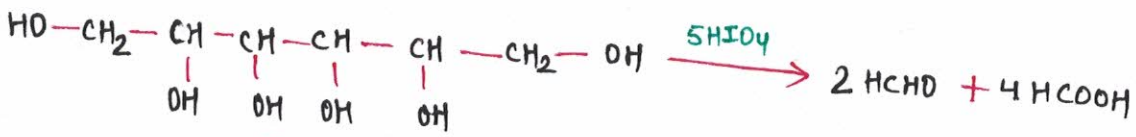


will not

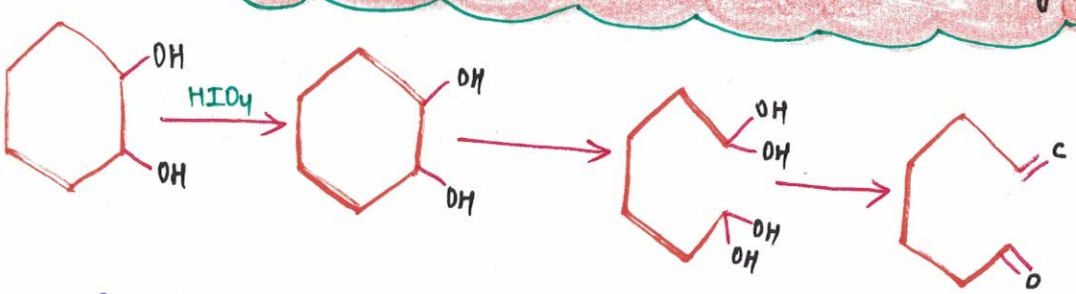


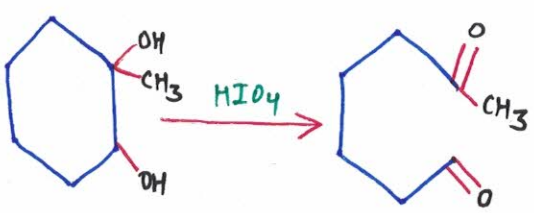


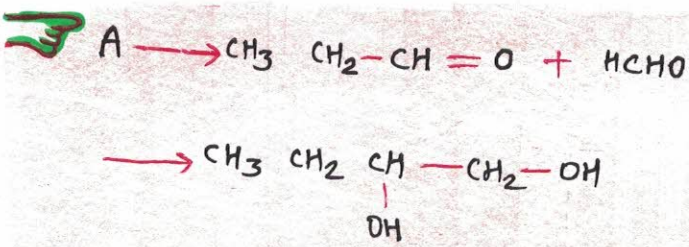


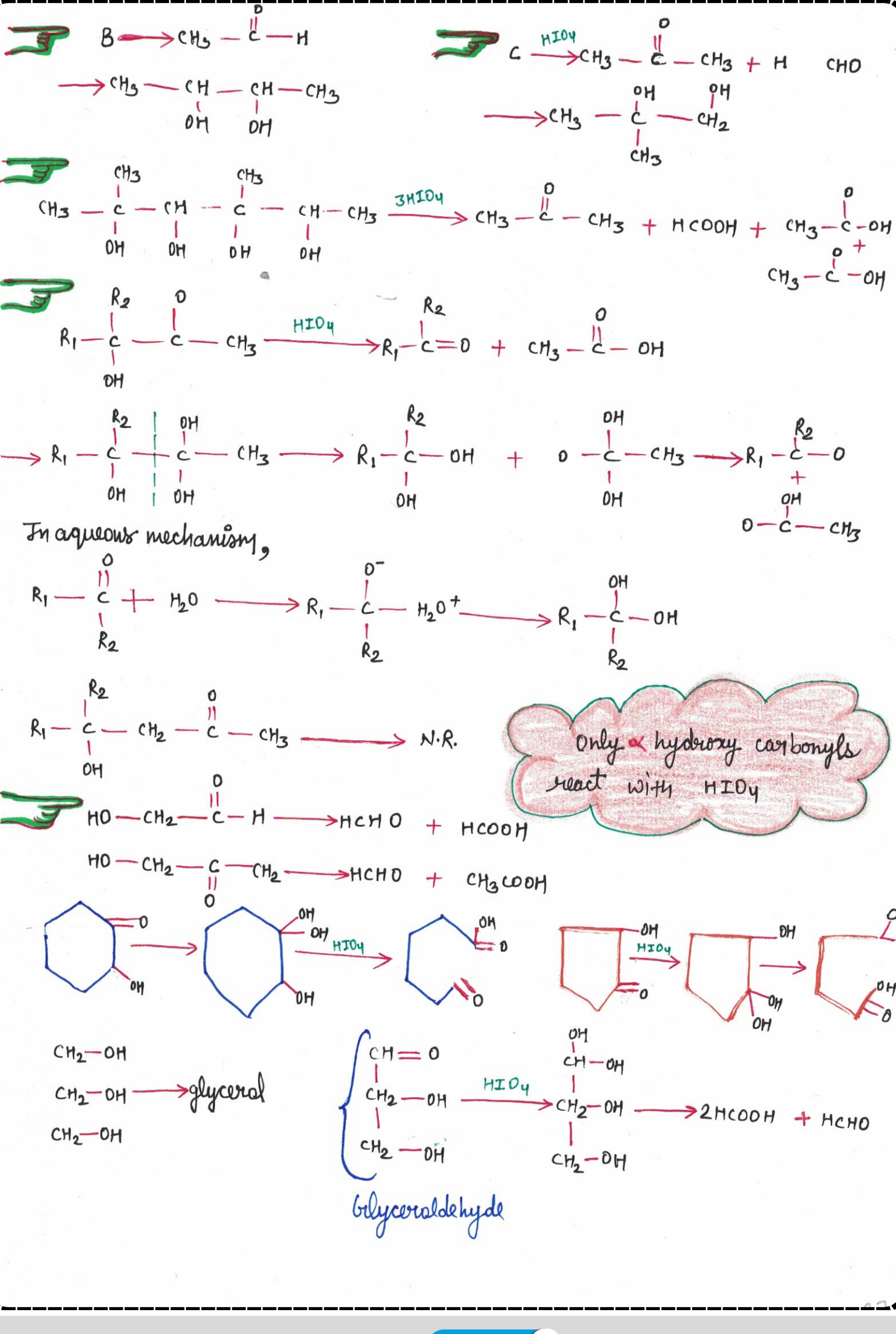


1 mole of HIO_4 is required for one cleavage

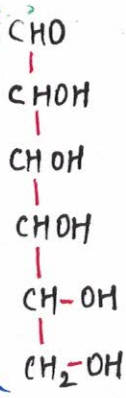






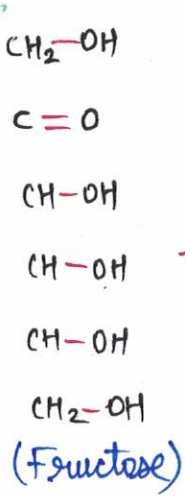


Glucose



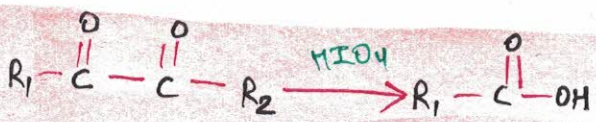
$\xrightarrow{}$ 5 HCOOH + HCHO

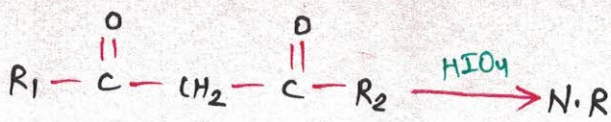
As Fructose gives CO_2 on reaction with HIO_4, this is a method to distinguish glucose/fructose. CO_2 will be released with effervescence.

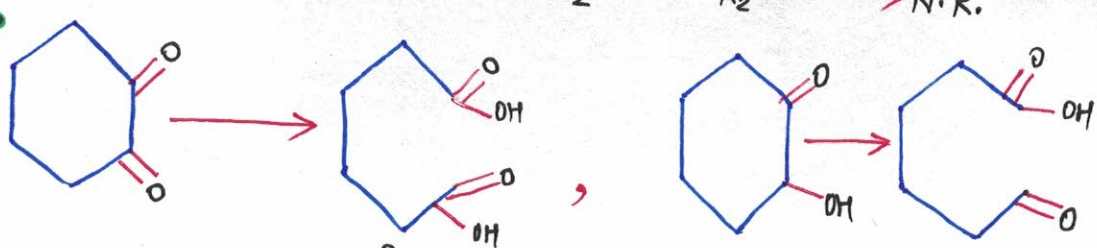


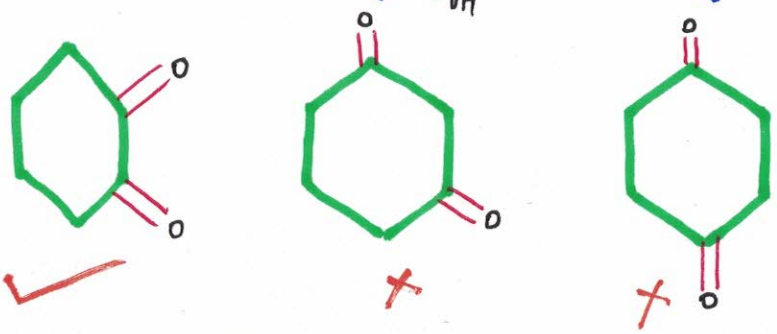
$\xrightarrow{5HIO_4}$ $2HCHO + CO_2\uparrow + 3HCOOH$

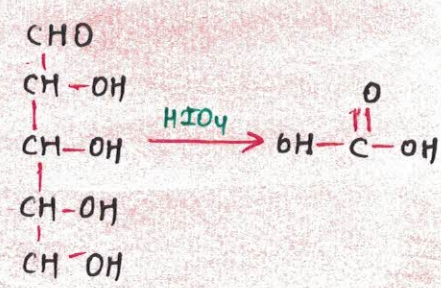
(Fructose)



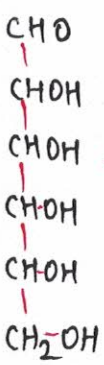








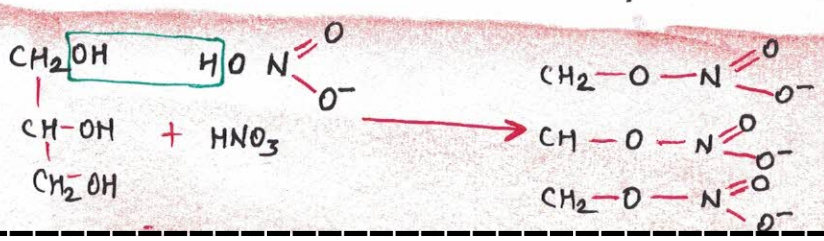
As % of nitro ↑ in a compound, its explosive nature ↑

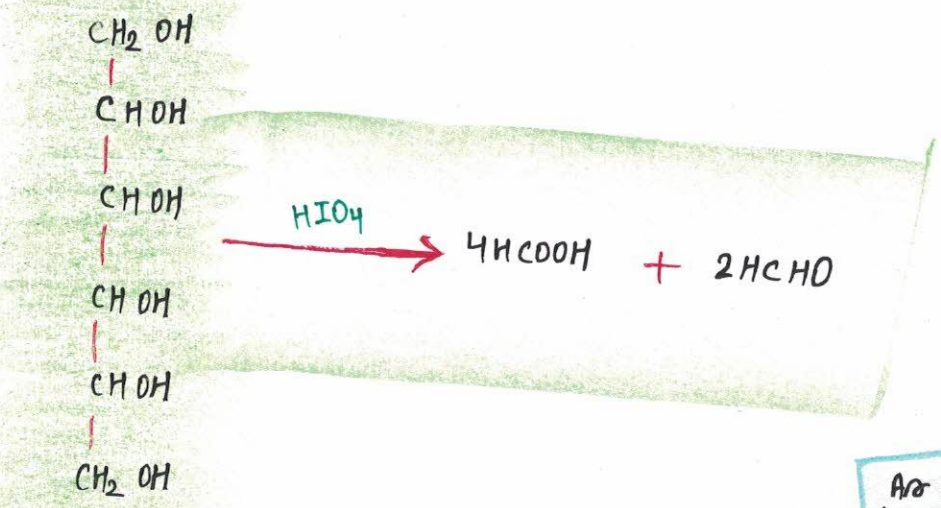


$\xrightarrow{}$ 5HCOOH + HCHO

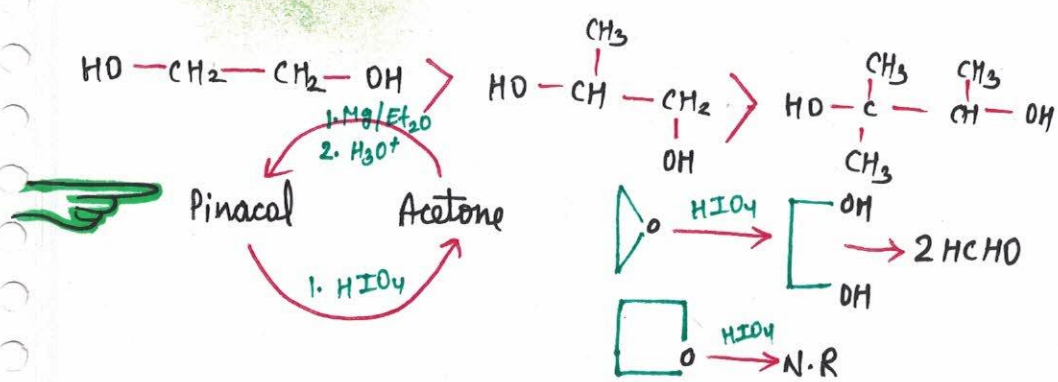
USES:-

1. Ethylene glycol used as anti freezing agent, used in polyster industries.
2. Glycerol is used to prepare glyceral trinitrate used as an explosive.

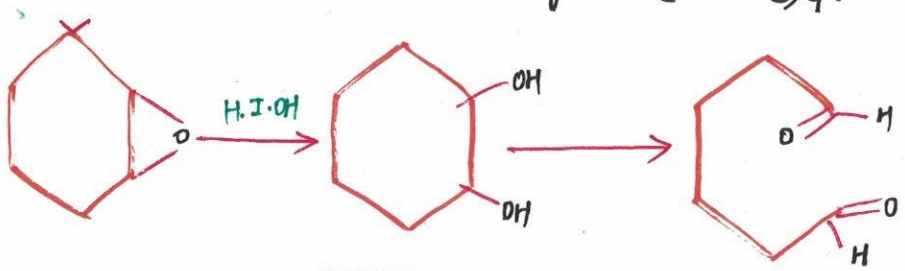




As crowding around glycol increases, rate of reaction decreases because in mechanism a cyclic compound is formed.



Reaction of HIO_4 can also be done by $Pb(OCOCH_3)_4$.



TEST FOR ALCOHOLS

1. By Lucas Reagent

→ $ZnCl_2$ + Conc. HCL is Lucas Reagent

$$R\,CH_2OH \xrightarrow{HX} R-CH_2^+ \longrightarrow R-CH_2-X \quad (3^\circ > 2^\circ > 1^\circ > Me)$$

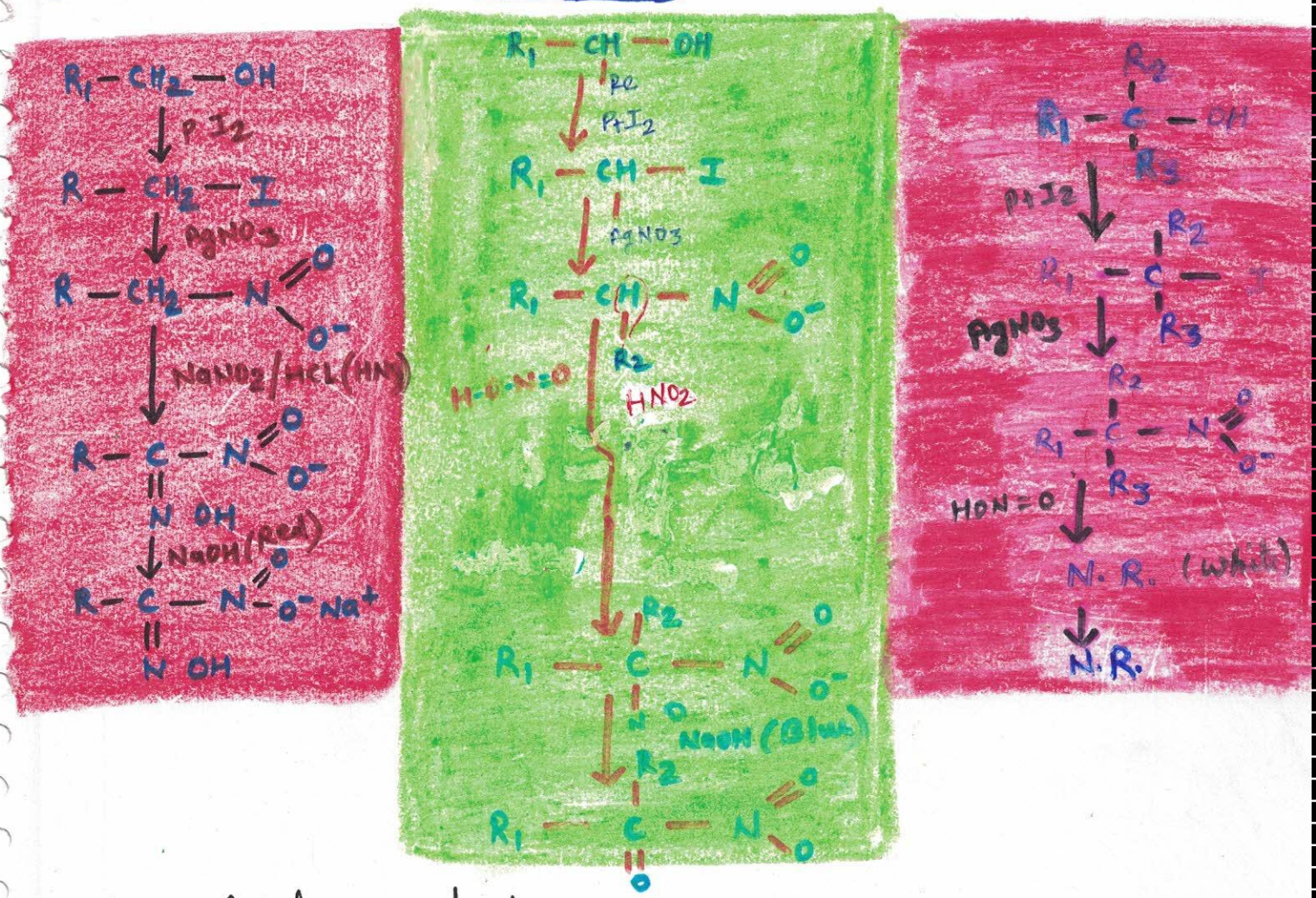
For HCL, we use $ZnCl_2$ as catalyst. R-Cl is less soluble than R-OH due to hydrogen bonding in R-OH.

We take a saturated mixture of R-OH & H_2O in a test tube. We add Lucas reagent. It changes into R-Cl giving a white emulsion.

If time taken is very less → tertiary alcohol.
If time taken is $5 < t < 10$ min → Secondary alcohol.
If time taken is $10 < t < 30$ min → Primary alcohol.

An opaque oily mixture is formed because soluble has become insoluble and hence the liquid has lost its transparence.

3. **By Victor Mayer Reagent**



Primary alcohol ⟶ red colour

Secondary alcohol ⟶ blue colour

Tertiary alcohol ⟶ white colour

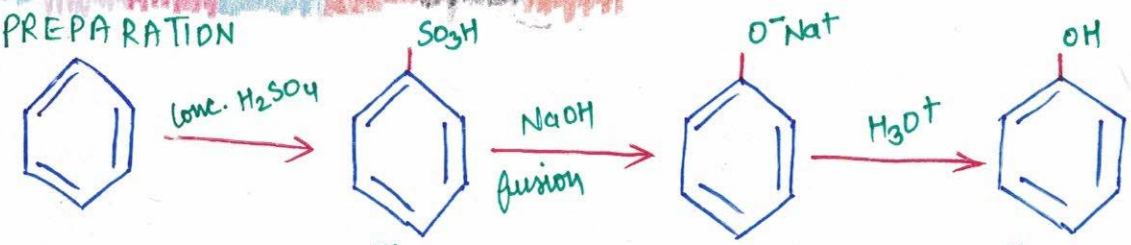
$(P\ I_2) \longrightarrow (AgNO_2) \longrightarrow HNO_2 \longrightarrow NaOH$

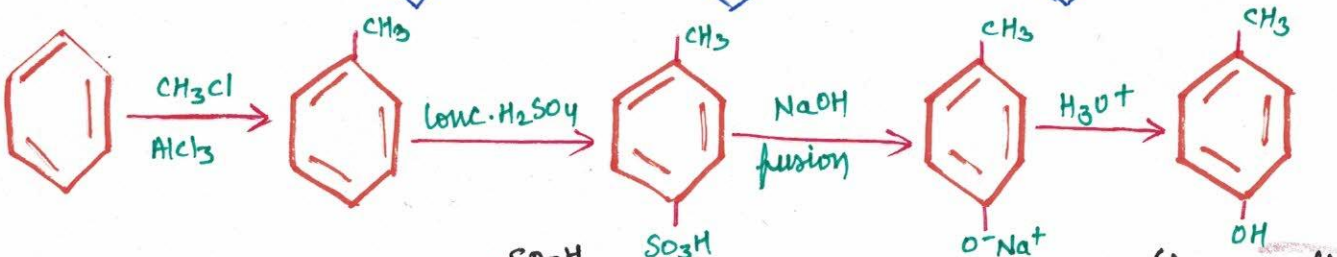
PHENOLS

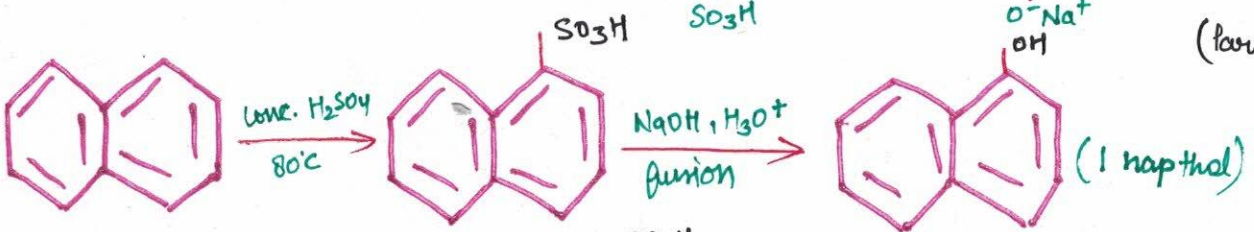
PHENOLS

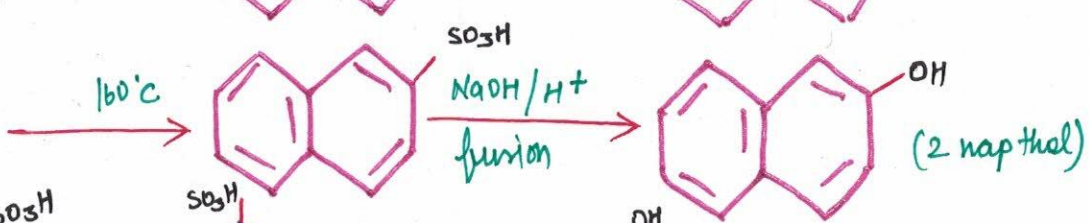
PREPARATION

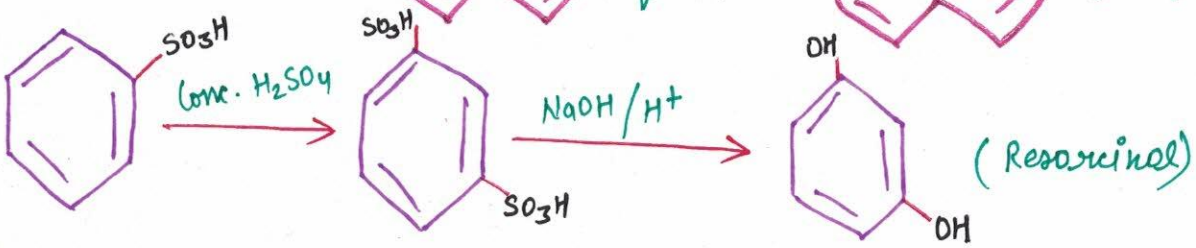
1.



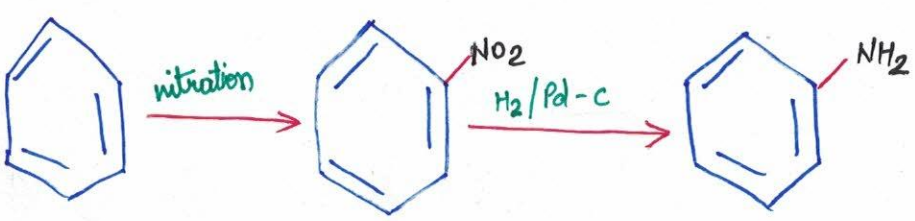


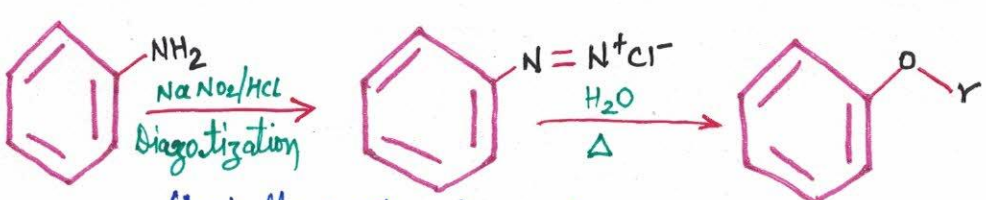




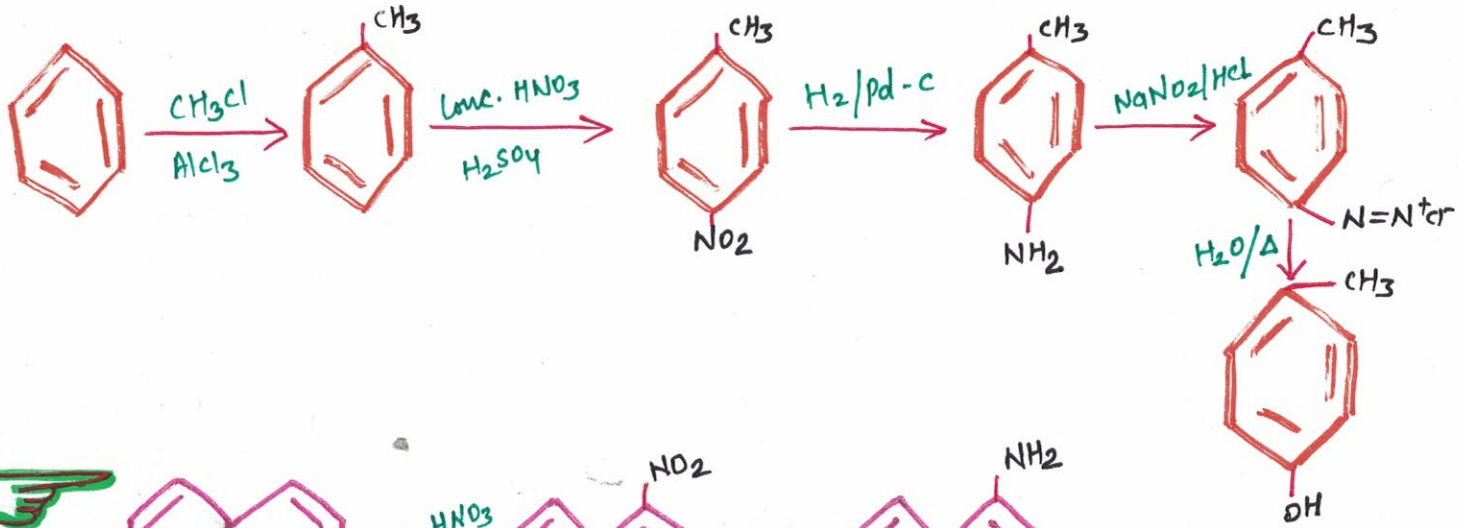


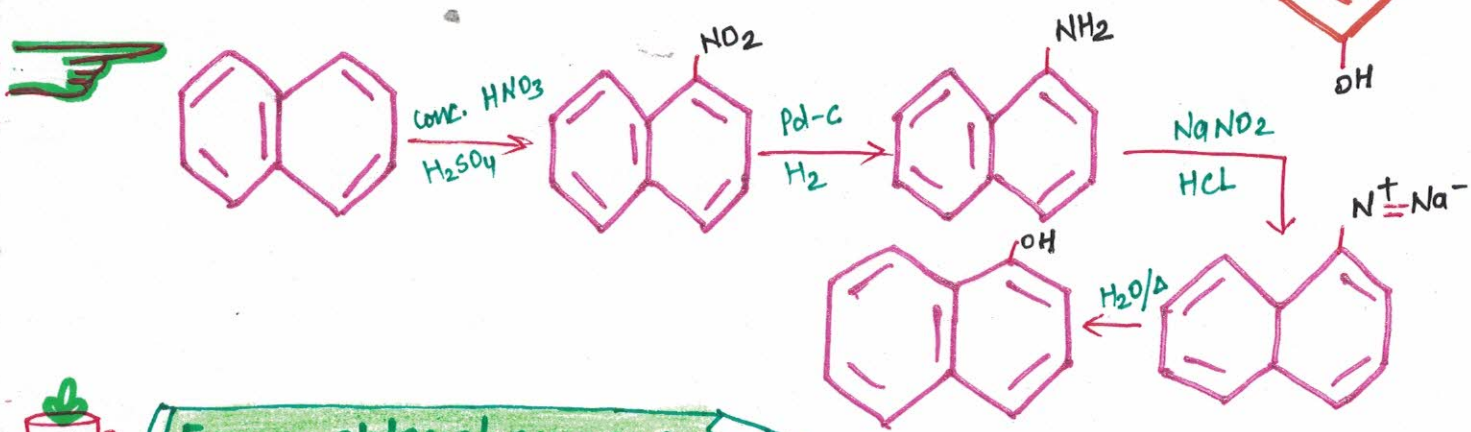
2. **From Nitrobenzene**





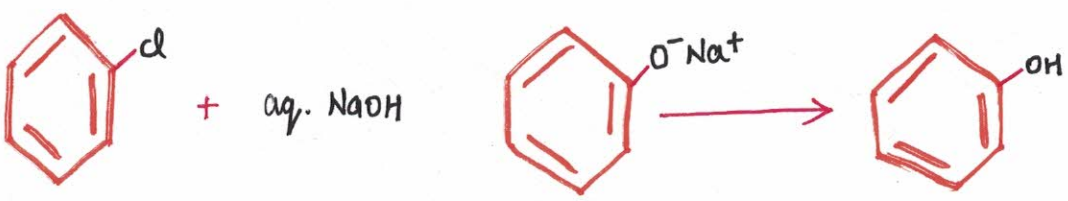
(basically reaction with HNO_2)



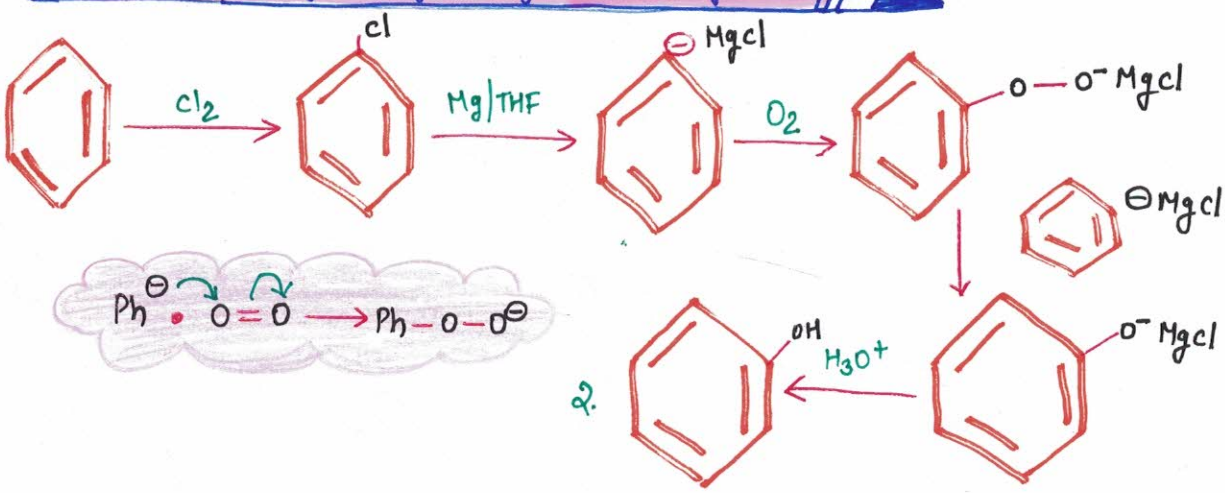


3. From chlorobenzene

a. Industrial Method

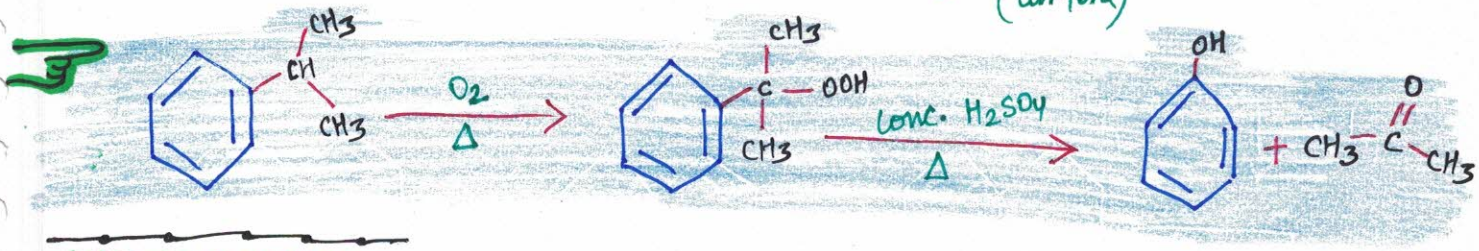


b. Lab method By using Grignard reagent

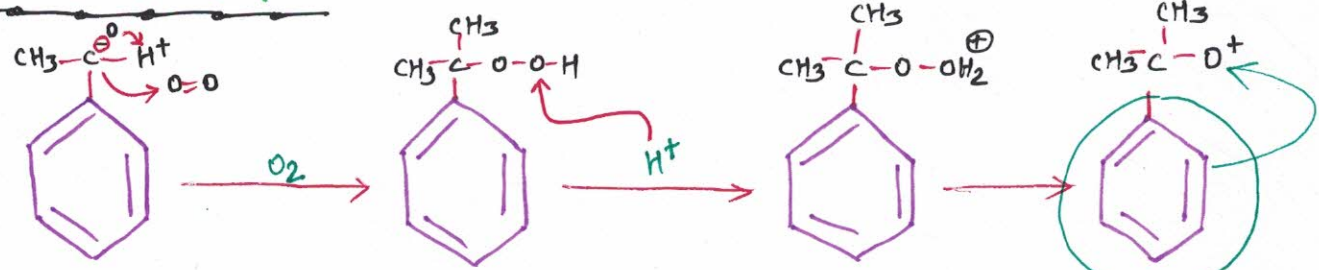


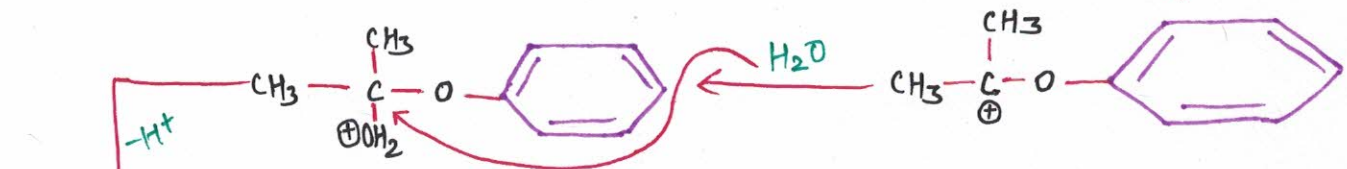
Grignard reagent not prepared in presence of O_2 as it changes to R—O—O⁻MgCl

4. **From cumene**

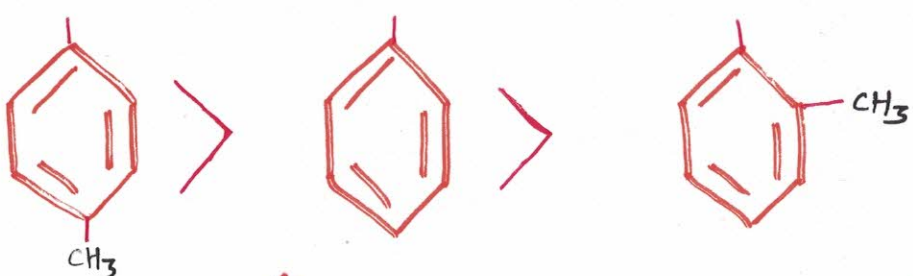


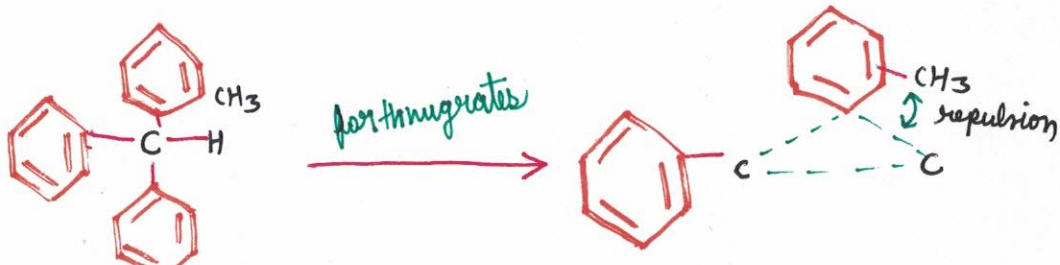
MECHANISM :-



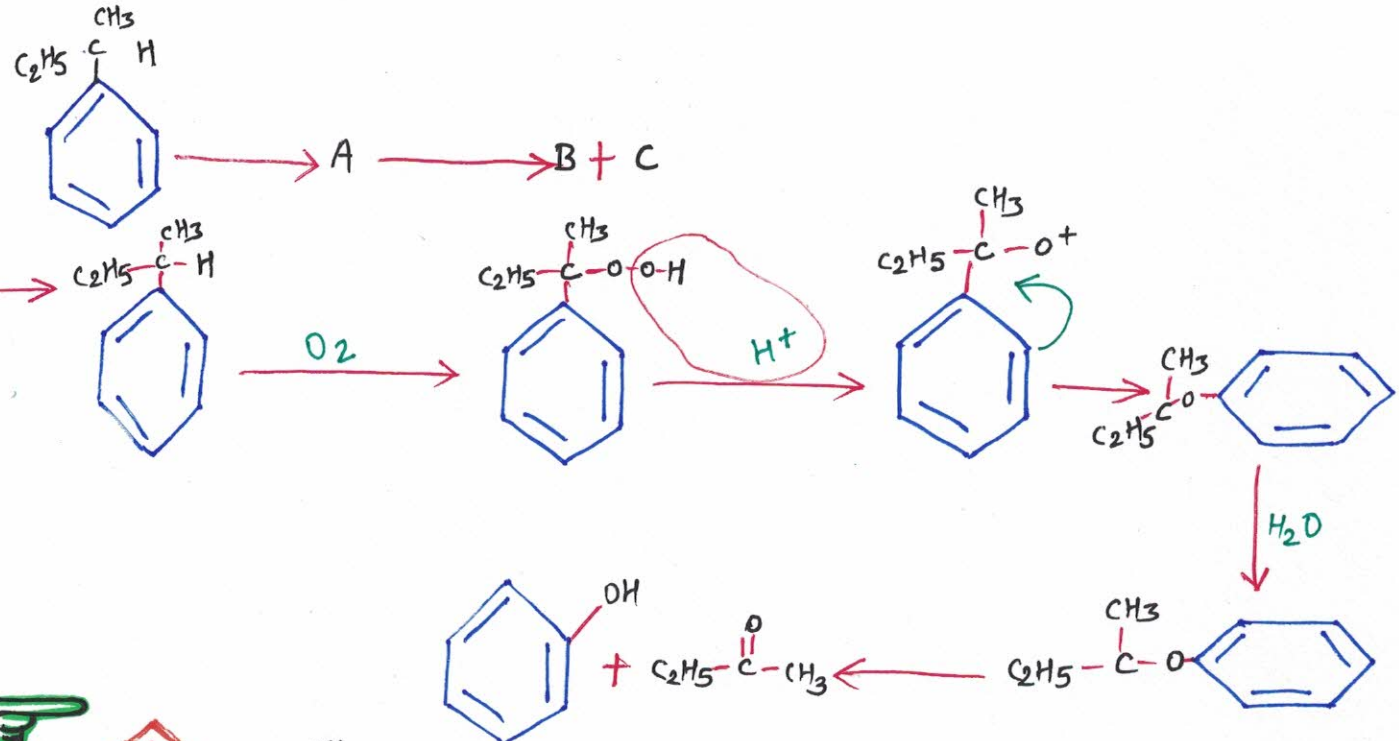


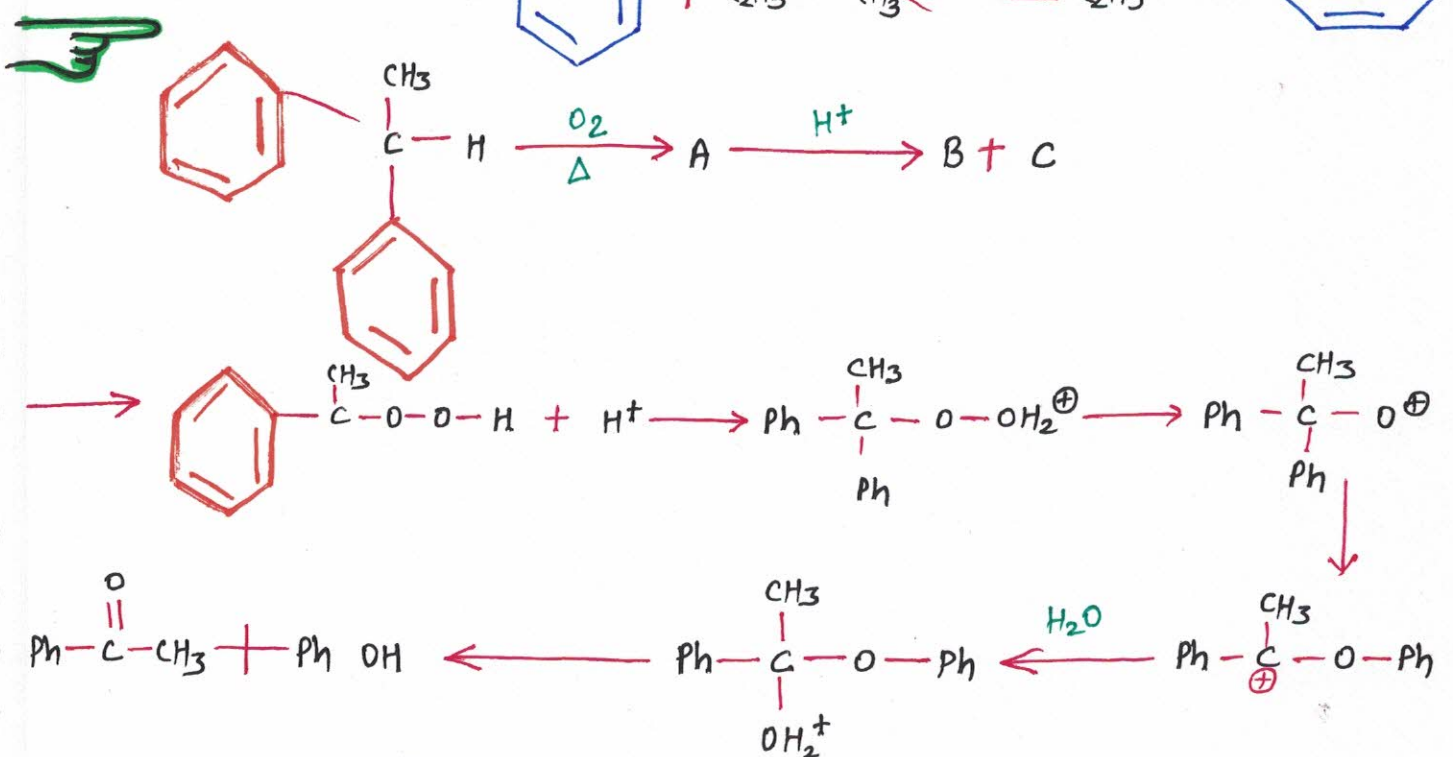
MIGRATION APTITUDE

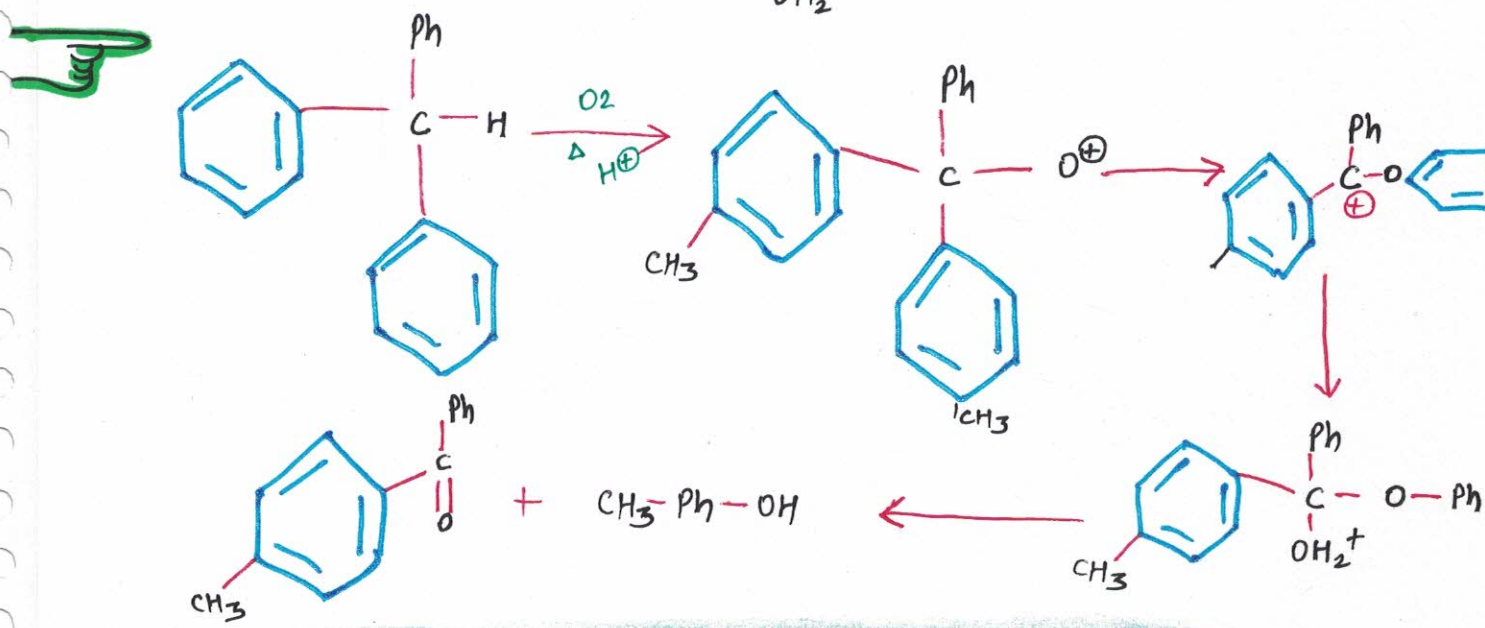




Hence para migrates more.



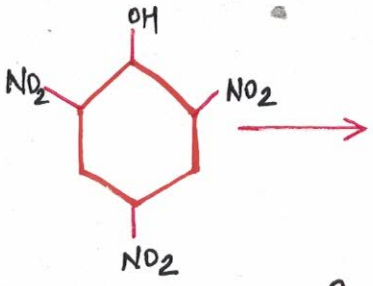




Always e⁻ rich will migrate to oxygen.

PROPERTIES OF PHENOLS

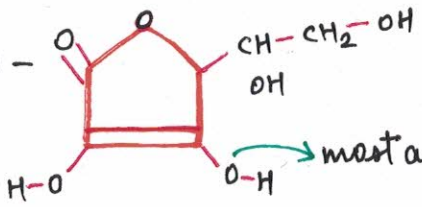
- Phenol is white crystalline solid (M.P ≈ 40°C)
  It is brown in color as it is in oxidised form.
- Phenol is soluble in hot water (Anilini is insoluble water)



→ Picric acid (only acid with no carboxylic acid)

Ascorbic acid has 4 hydroxy groups.
Picric acid has 3 nitro groups.

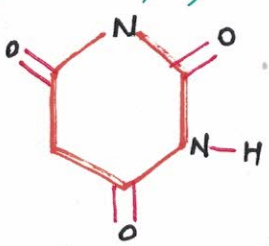
ASCORBIC ACID –



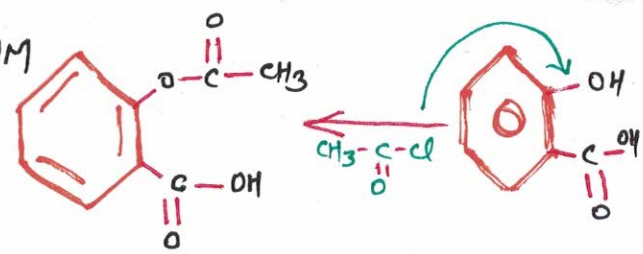
→ most acidic hydrogen

(Vitamin-C)

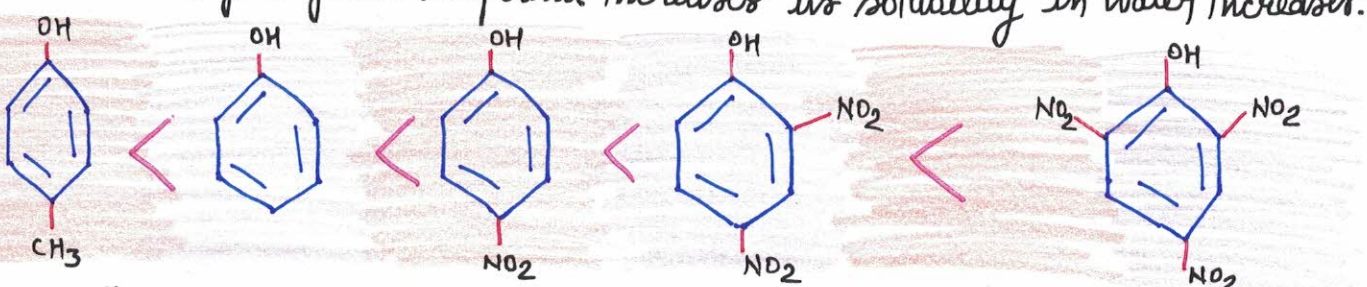
BARBITRIC ACID



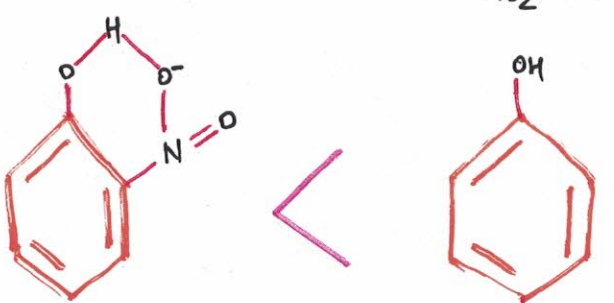
ASPIRIUM



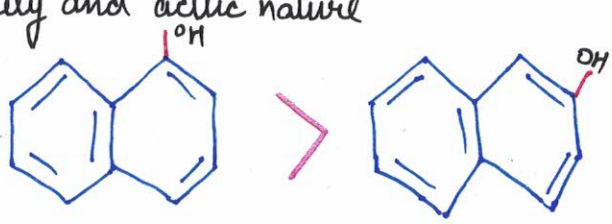
As acidic nature of organic compound increases its solubility in water increases.



Solubility and acitic nature



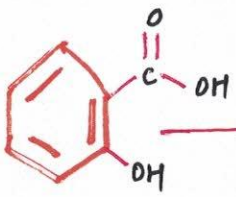
acidic nature
solubility



Solubility &
Acidic nature

Phenols have anti fungal & anti bacterial properties. Hence used as disinfectants and anticeptics.

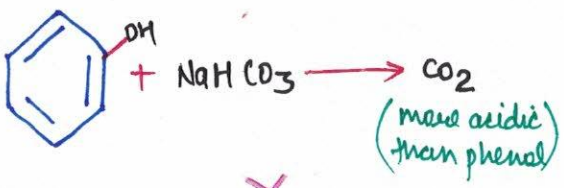
Phenol at low conc^n → Anticeptic
Phenol at high conc^n → disinfectant



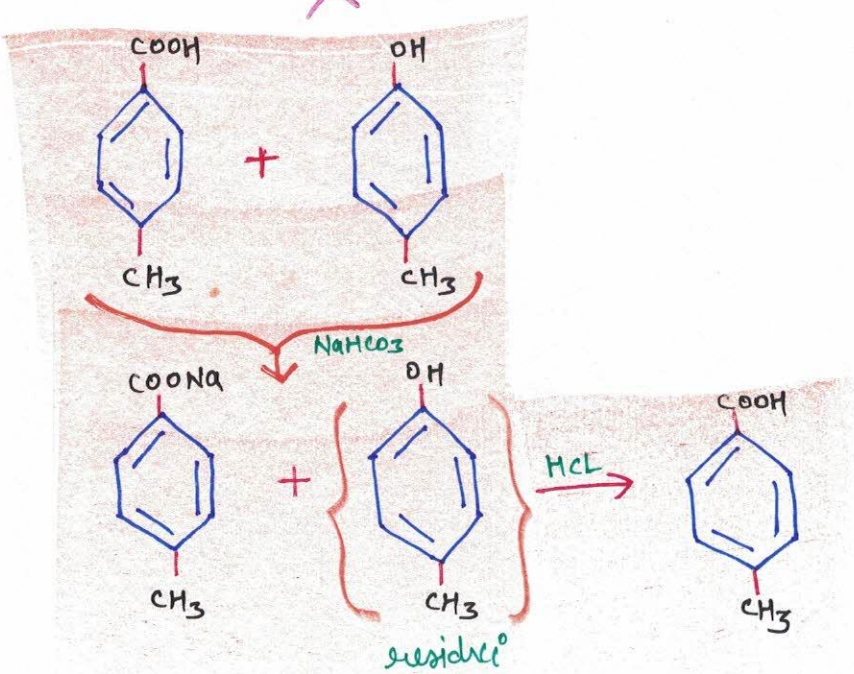
→ salicylic acid (Highly used as anti-fungal)

Shampoos mostly contain phenols.

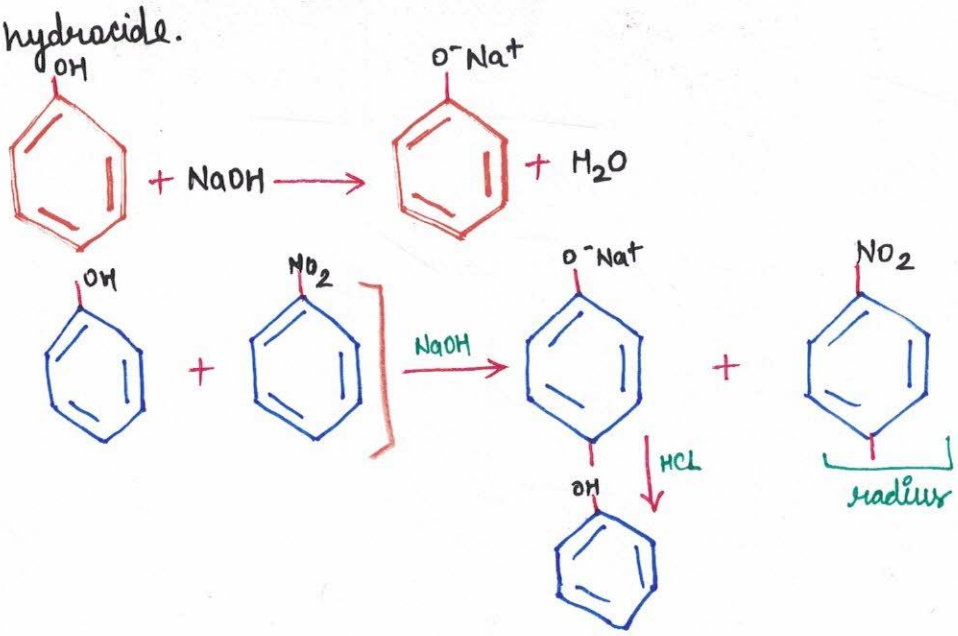
Phenols are more acidic than water.



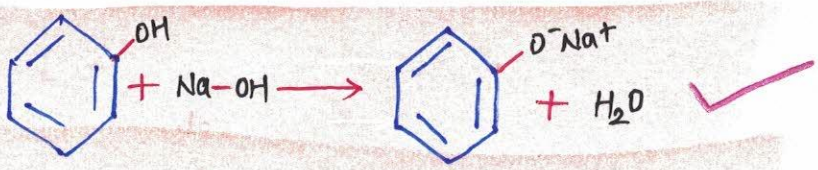
$RCOOH + NaHCO_3 \rightarrow RCOONa + CO_2 \uparrow$ ✓

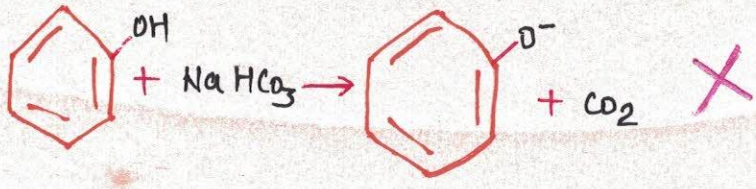


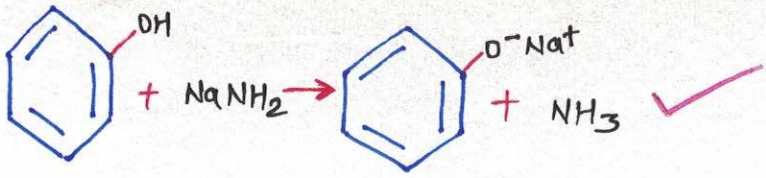
Phenols do not dissolve in sodium bicarbonate but phenols react with sodium hydroxide.

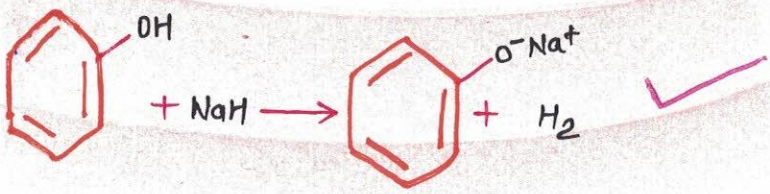


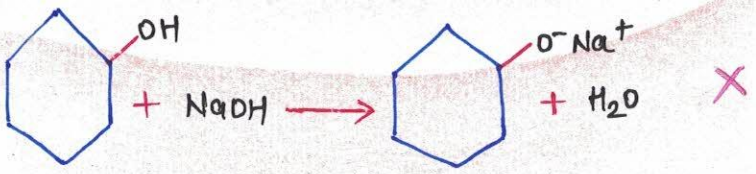
To distinguish between carboxylic acid & phenols we use $NaHCO_3$.

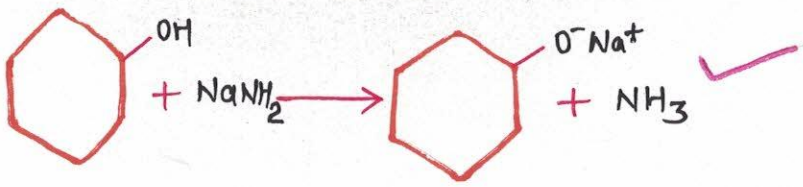


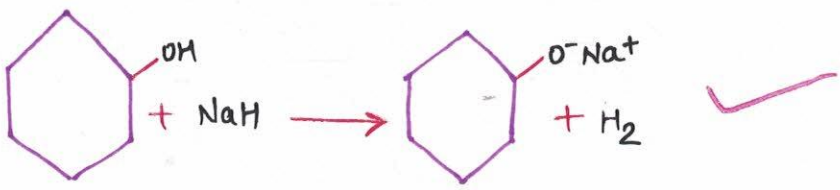












$CH \equiv CH + NaOH \longrightarrow CH\ C^-Na^+ \quad H_2O$ ✗

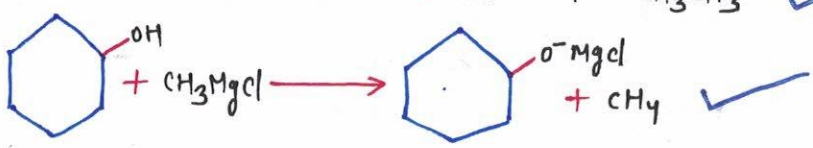
$CH \equiv CH + NaOEt \longrightarrow CH\ C^-Na^+ \quad EtOH$ ✗

$CH \equiv CH + NaH \longrightarrow CH\ C^-Na^+ \quad H_2$ ✓

$CH \equiv CH + NaNH_2 \longrightarrow CH\ C^-Na \quad NH_3$ ✓

$CH \equiv CH + CH_3MgCl \longrightarrow CH\ CMgCl \quad CH_4$ ✓

$CH \equiv CH + CH_2CH^-Li^+ \longrightarrow CH\ CLi \quad CH_3CH_3$ ✓

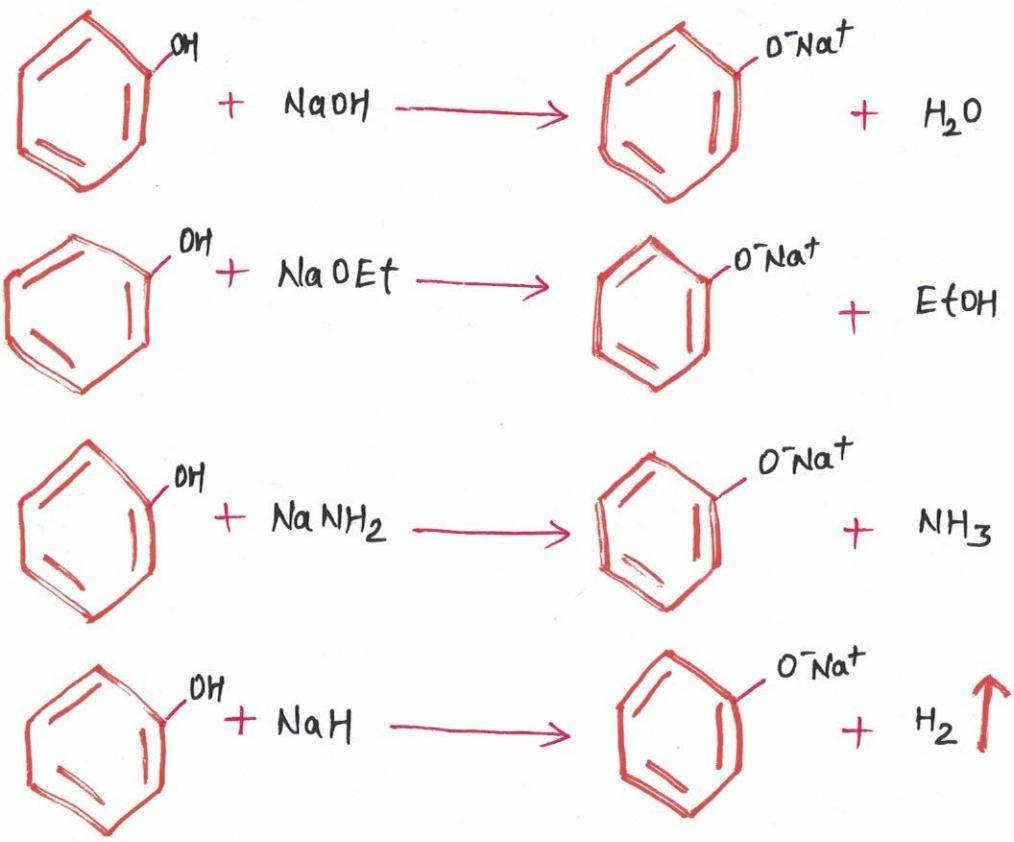


Properties of phenols can be devided into two groups –

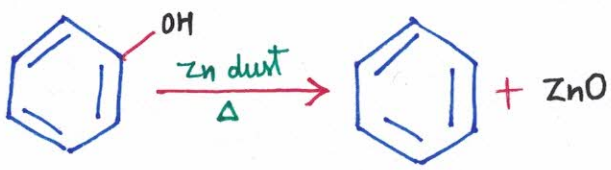
1. Reactions due to –OH group
2. Reactions due to ring substitution

1. Reactions due to –OH group

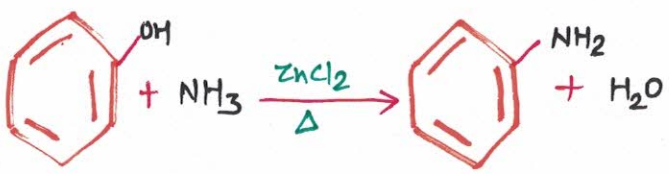
i. SALT FORMATION



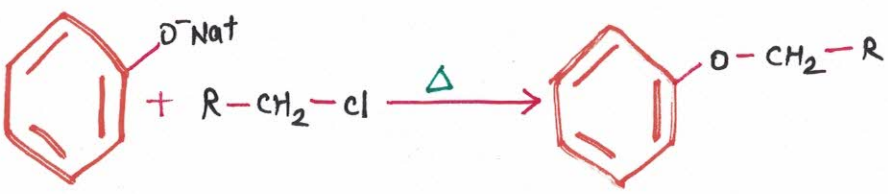
ii. WITH Zn DUST ⇒



iii. WITH NH_3 ⇒

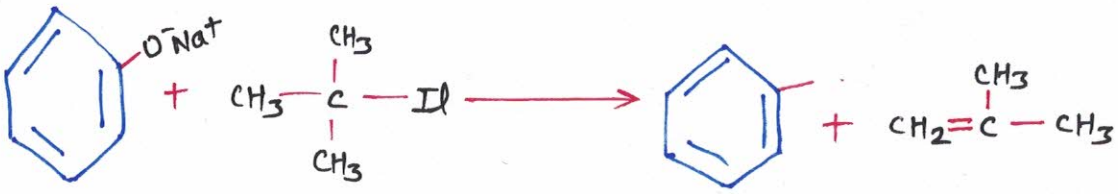


iv. WILLIAMSON'S SYNTHESIS

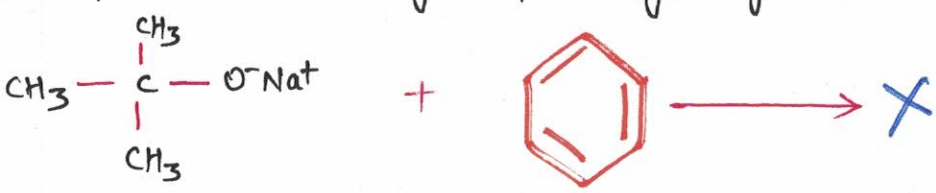


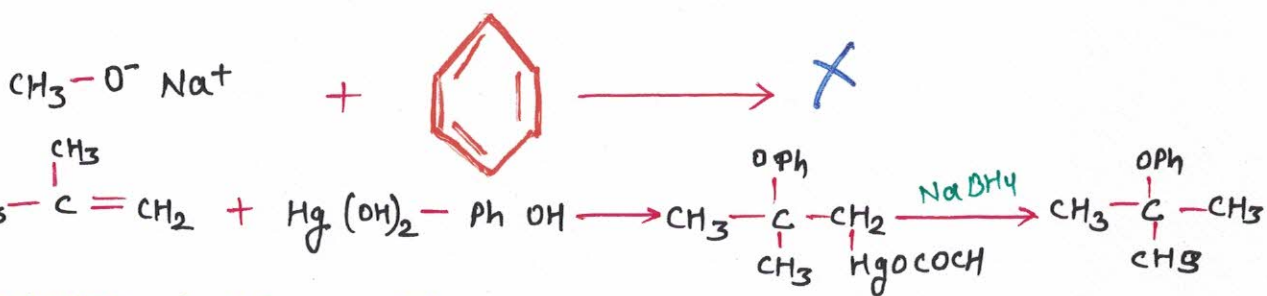
This is a method to prepare ethers.

(Anisole)

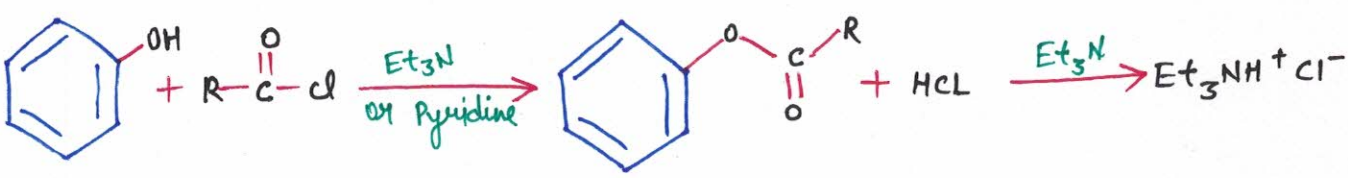


Substitution is to be done only on primary alkyl halides.

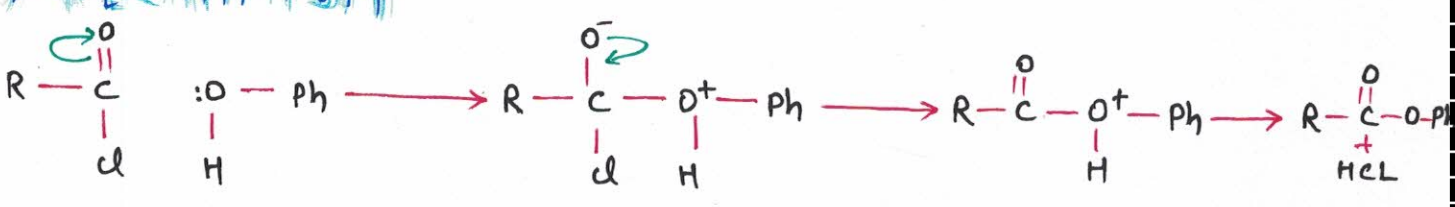


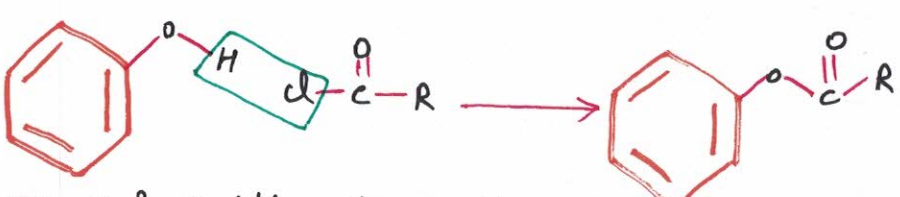


V. ACYLATION OF PHENOL

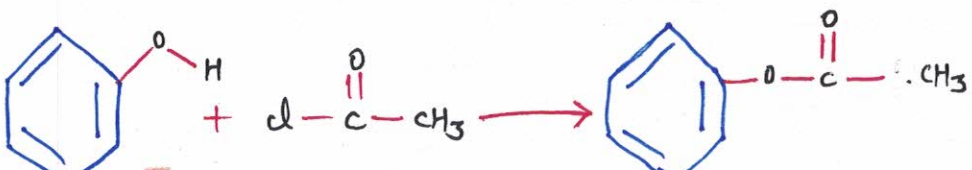


MECHANISM

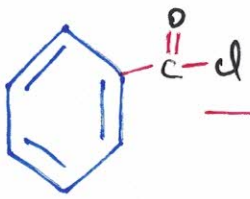




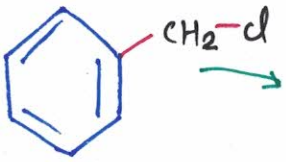
Et_3N & Pyridine act as acid absorbers.



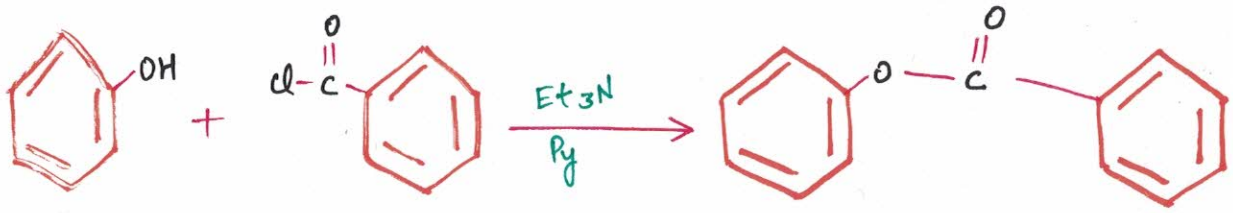
This process is called acetylation



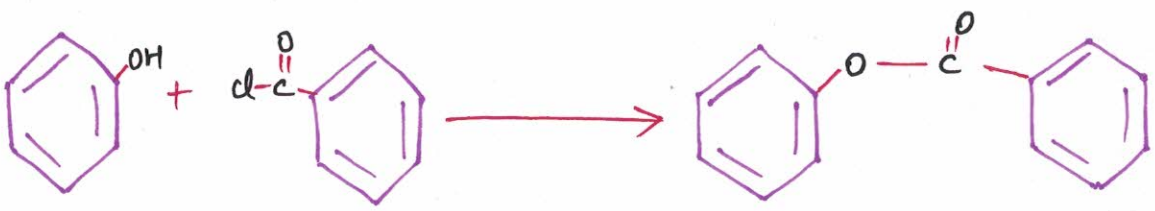
Benzoyl chloride



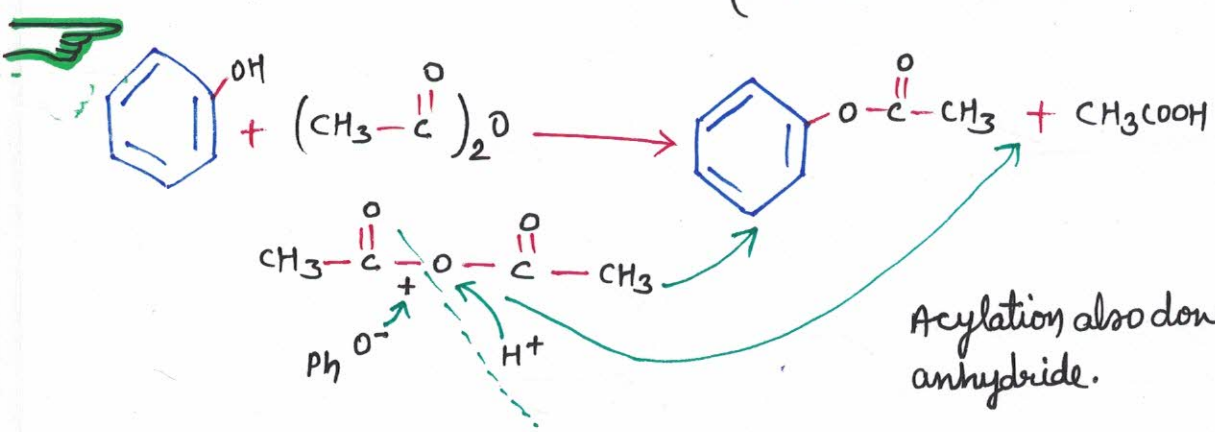
Benzyl chloride



Benzoylation of phenols is known as Schotten Baumann Reaction.



(Schotten Baumann Reaction)

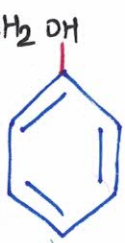


Acylation also done by acetic anhydride.

REACTION WITH $FeCl_3$ (Lenols always give this test)

+ $FeCl_3$ → Deep violet colour

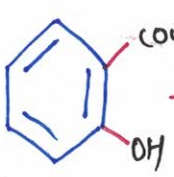
This is a test for phenol.



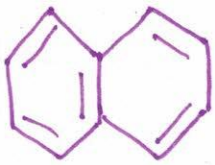
→ does not dissolve in NaOH & will not give test with $FeCl_3$

→ Will give test with $FeCl_3$ & will dissolve in NaOH

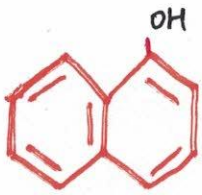
→ Will not give test with $FeCl_3$



→ Will give test with $FeCl_3$



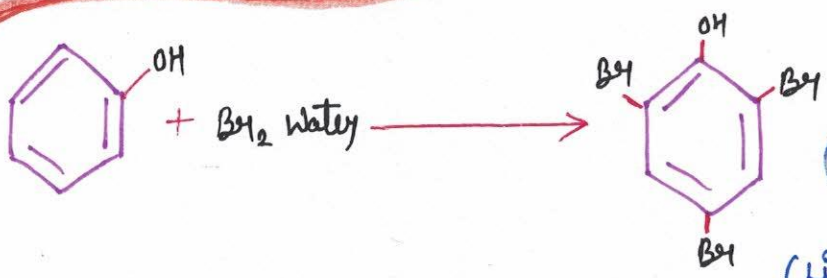
will not give test with $FeCl_3$ but



(napthol) will give test with $FeCl_3$

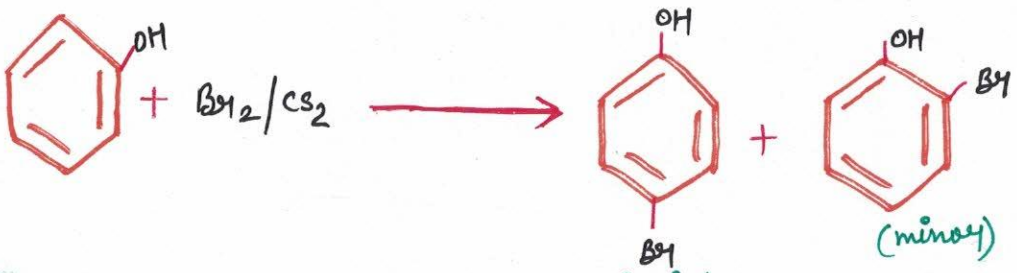
2. Reactions due to ring substitutions

i HALOGENATION



(2,4,6, tribromo phenol)

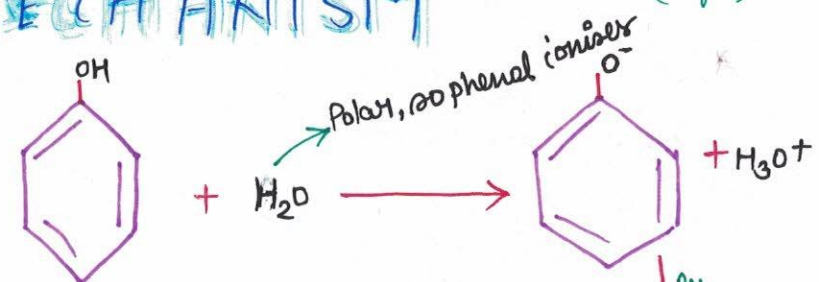
(Light yellow ppt.)



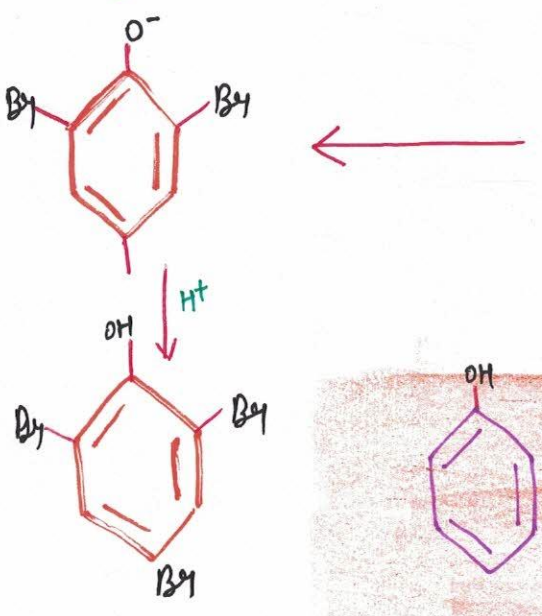
(major)

(minor)

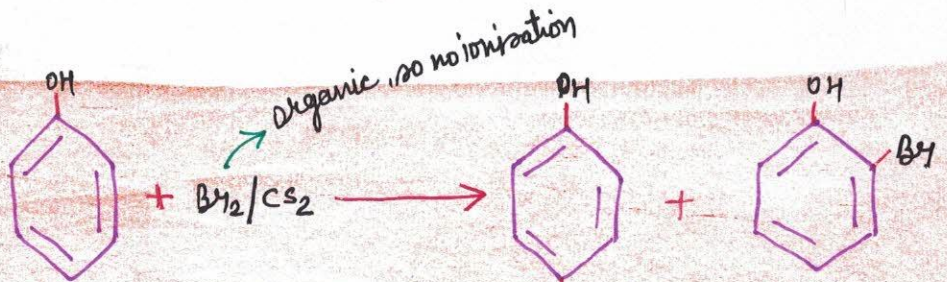
MECHANISM



Polar, so phenol ionises

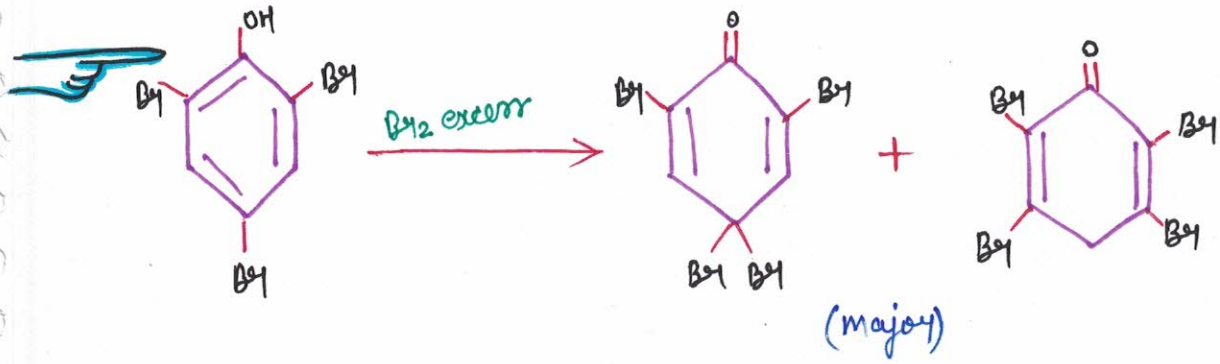


O^- is strong releasing group so ring still activated & bromination continued upto 3 times.

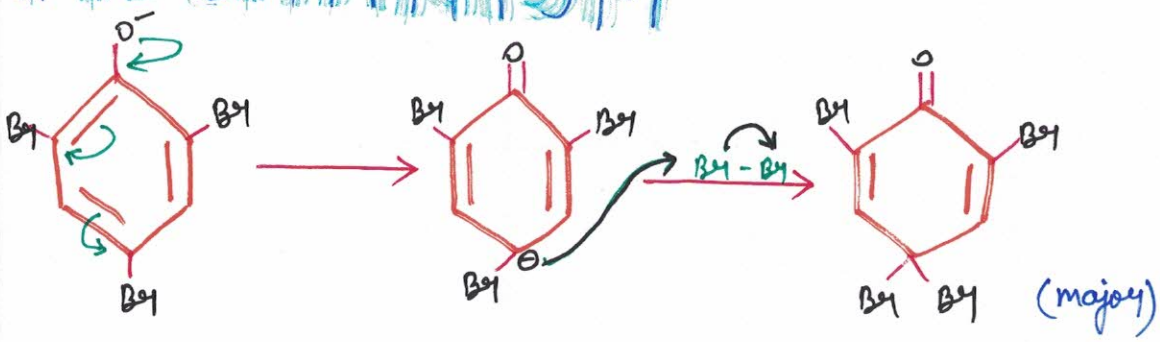


Organic, so no ionisation

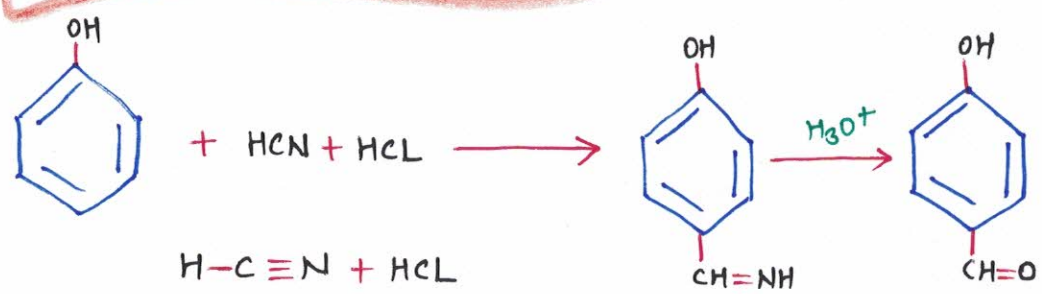
So in CS_2 monobromination occur but in Br_2 water, tribromination occurs.



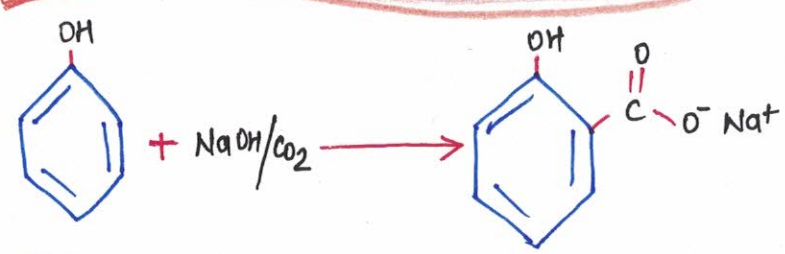
MECHANISM



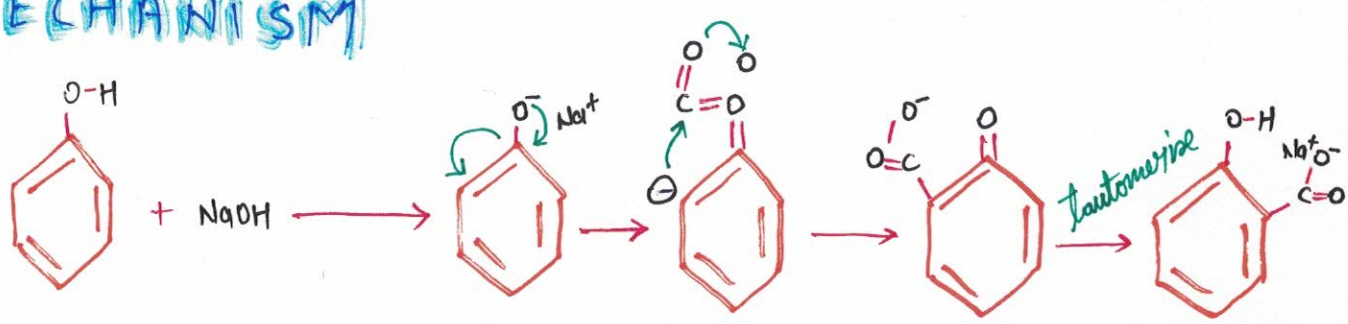
(ii) Gattermann Aldehyde Synthesis

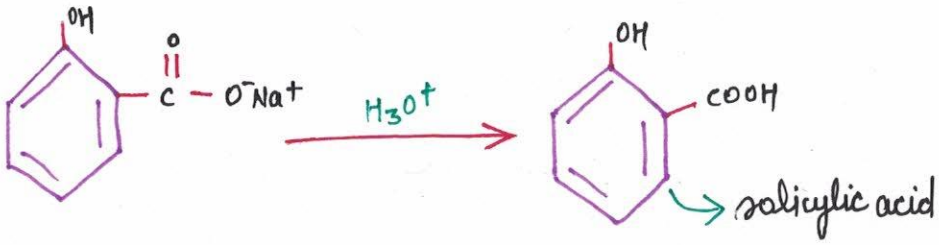


(iii) Kolbe's Schmidth Reaction

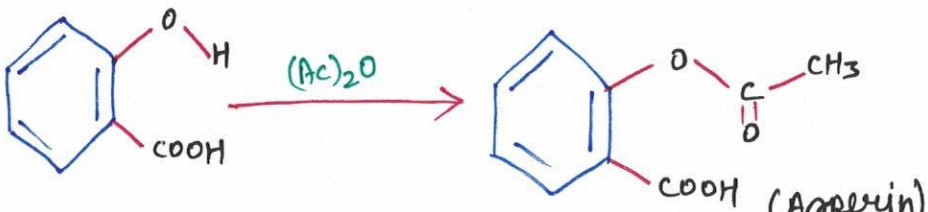


MECHANISM





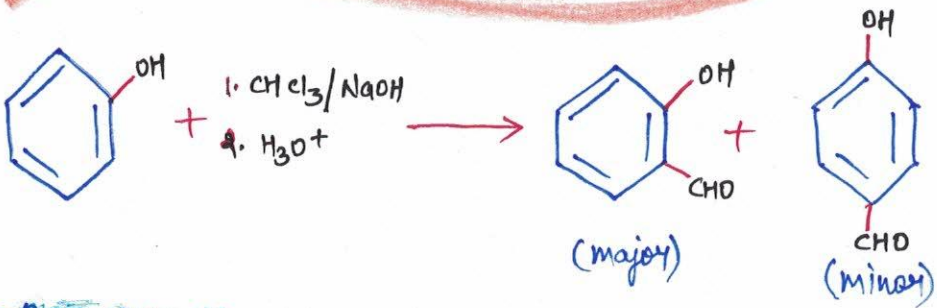
Conversion of phenol into salicylic acid



(Aspirin)

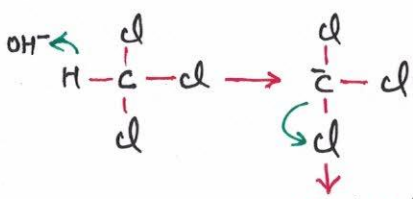
Aspirin makes blood thin and blood clothing does not occur Recommended for heart patients.

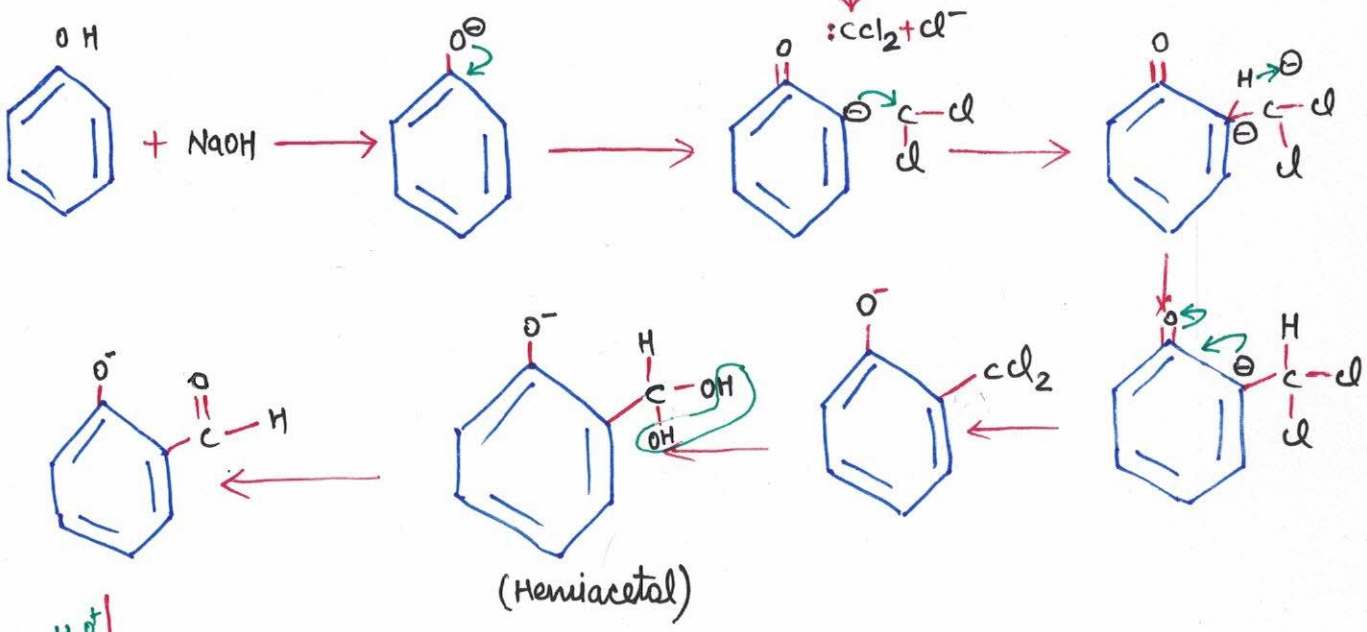
(iv) Rimer Teimann Reaction



MECHANISM

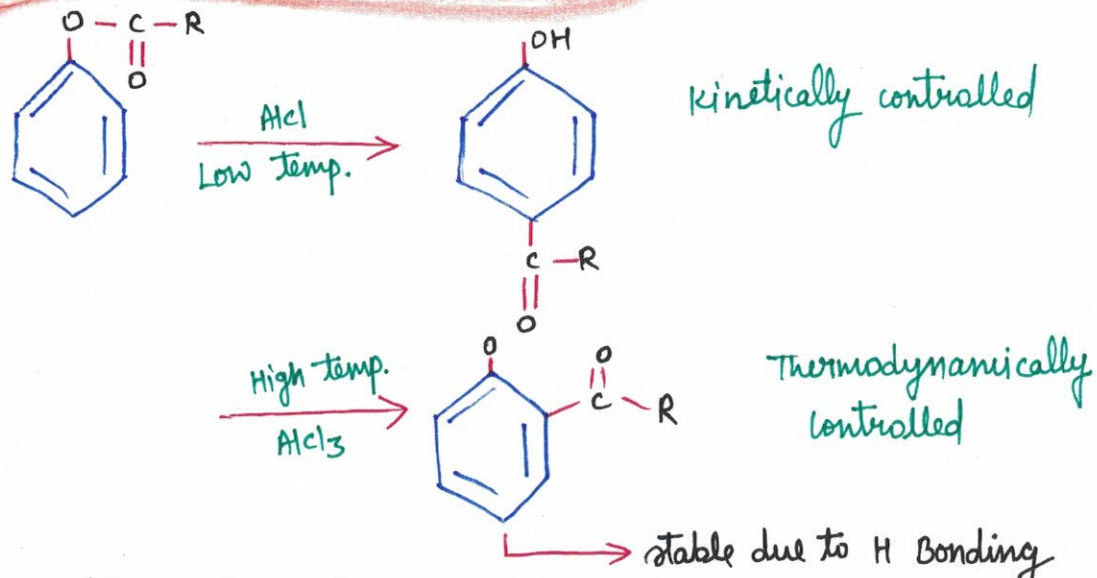
$CHCl_3 + OH^- \rightarrow :CCl_2$ carbine





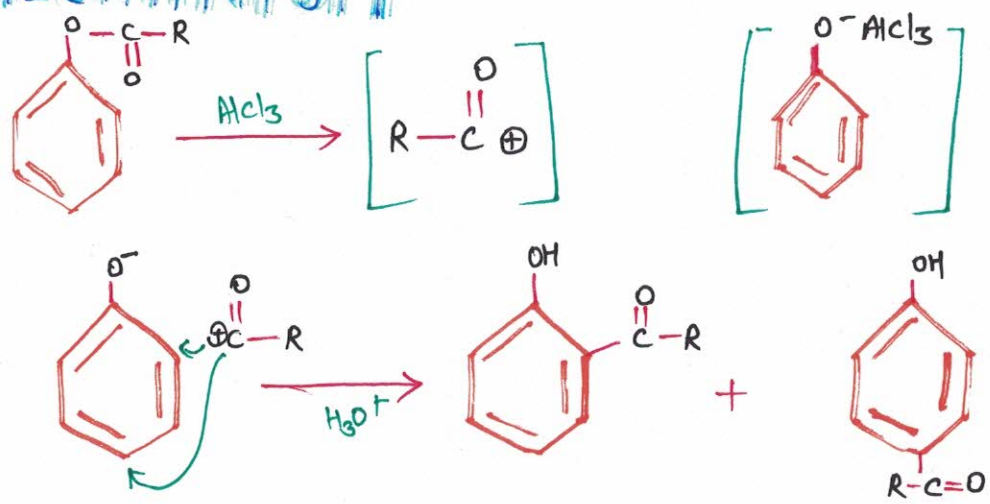
(Hemiacetal)

V Fries Rearrangement

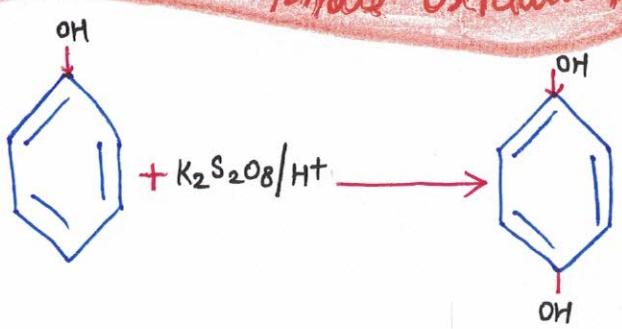


The reaction of ether with $AlCl_3$ at high & Low temp to form ortho acyl & para acyl is called Fries rearrangement.

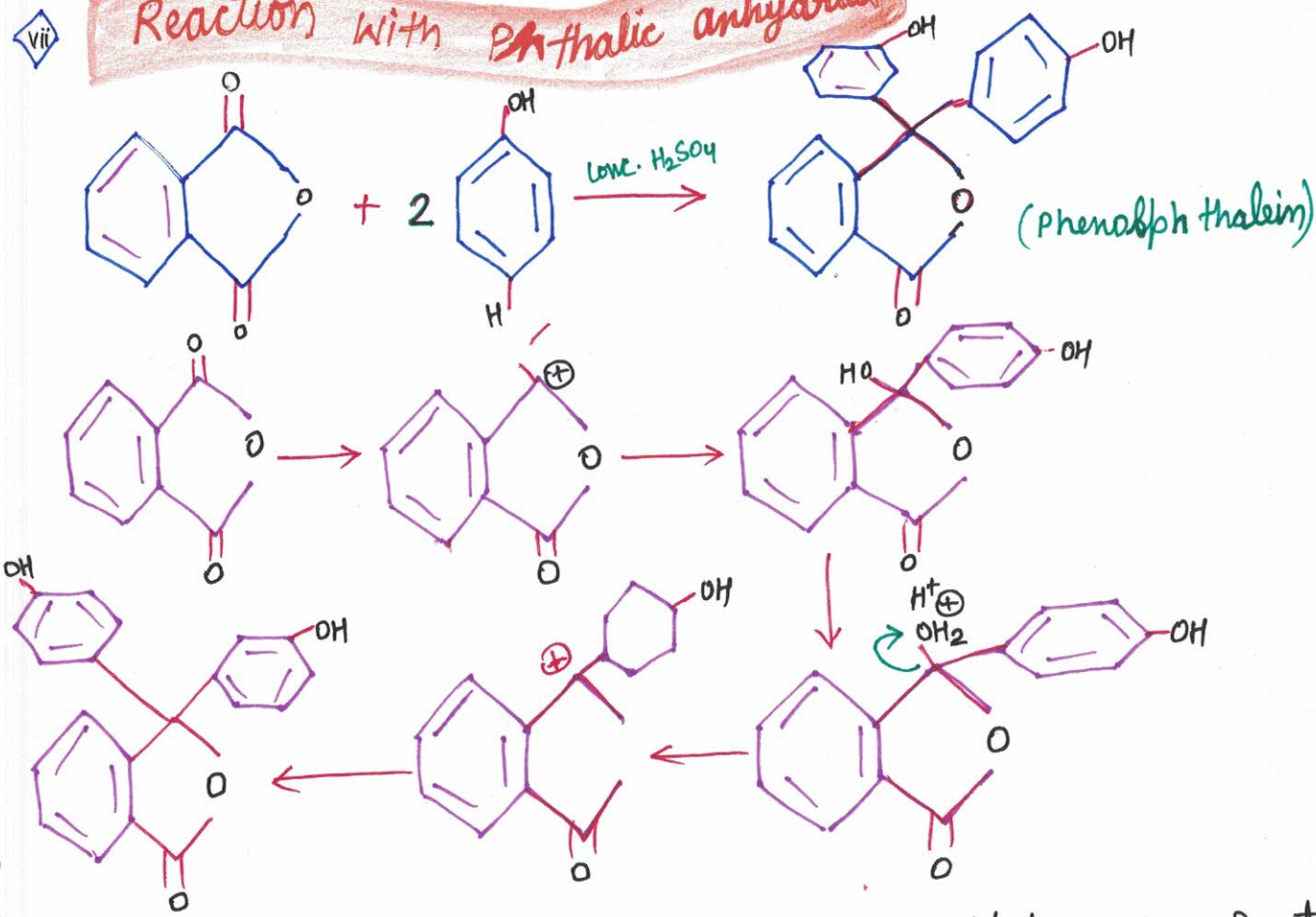
MECHANISM



VI Elbs Persulphate oxidation

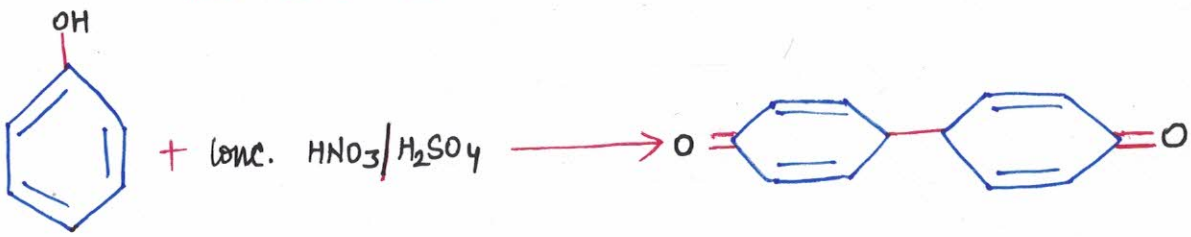


(vii) **Reaction with Phthalic anhydride**

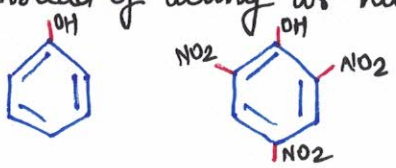


It is used as an indicator in acid base for strong acid / strong base & strong base / weak acid titration.

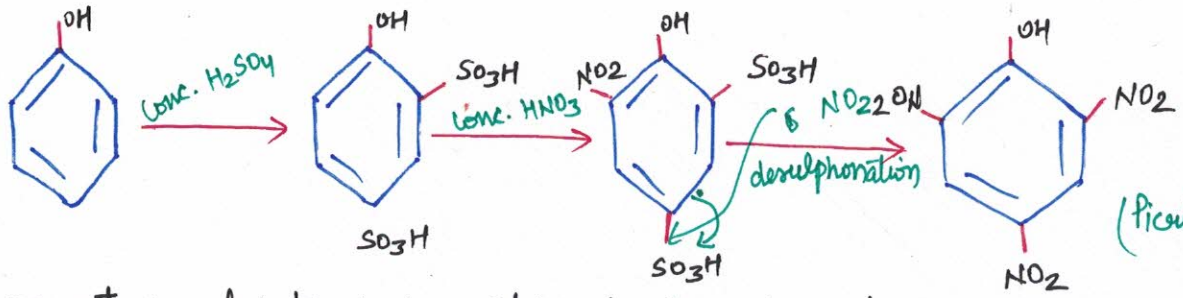
Nitration of Phenols



Phenol does not undergo nitration as the ring is highly activated and HNO_3 instead of acting as nitrating agent acts as oxidising agent. But, to convert

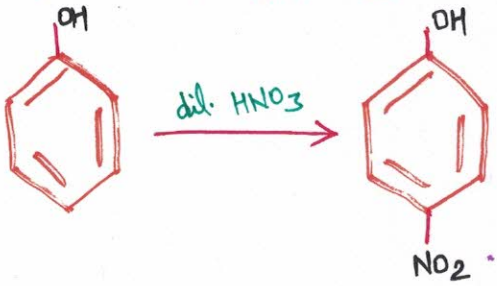


we use,



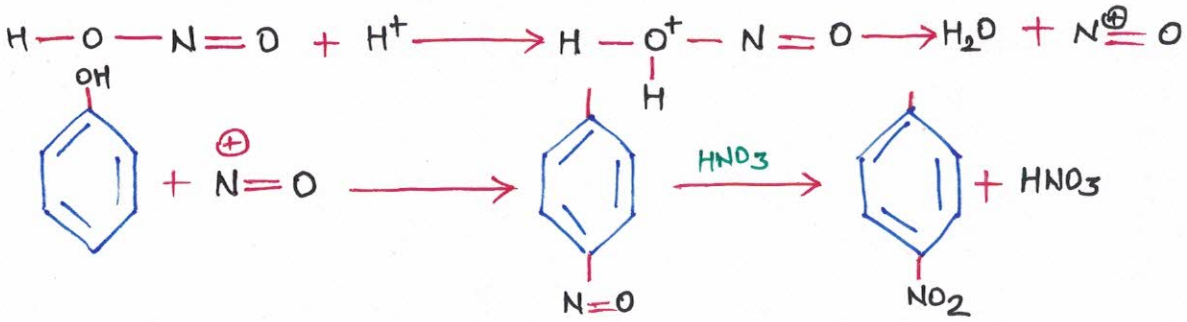
we convert phenol into picric acid by first sulphonating it and doing nitration & then desul-phonating again and nitrating.

REACTION WITH DILUTE HNO_3



MECHANISM

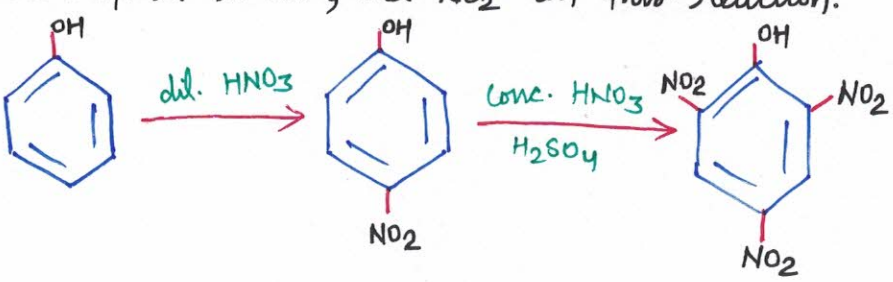
There is never 100% pure HNO_3 available as they get reduced in coming in contact with air or container. so, HNO_3 gets converted to HNO_2.

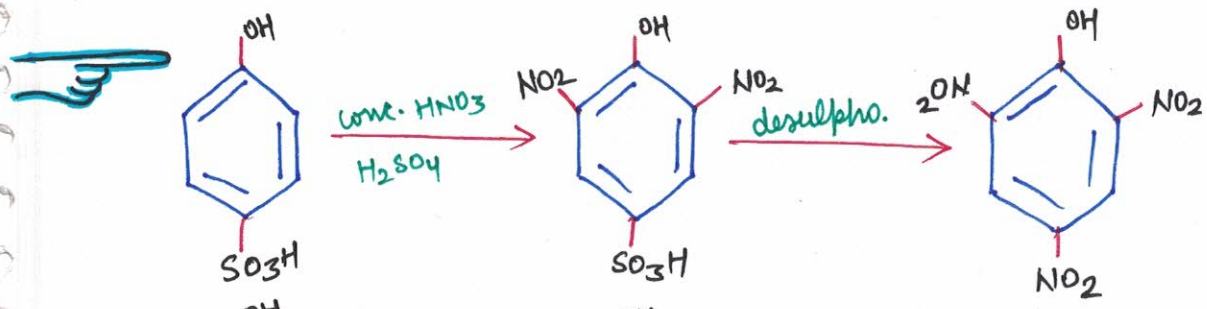


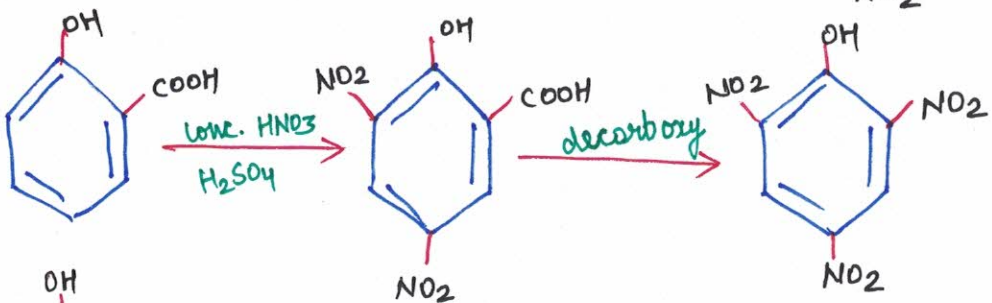
NO_2^+ is a strong electrophile than NO^+

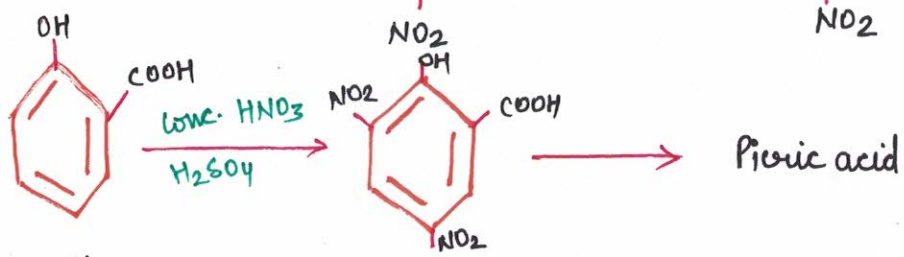
HNO_2 has been regenerated again.

X + dil. HNO_3, the reaction is Nitrososionation followed by oxidation. The electrophile is NO^+, not NO_2^+ in this reaction.

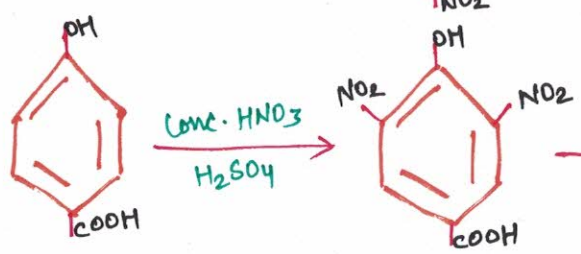




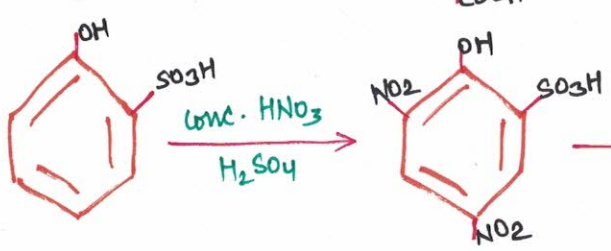




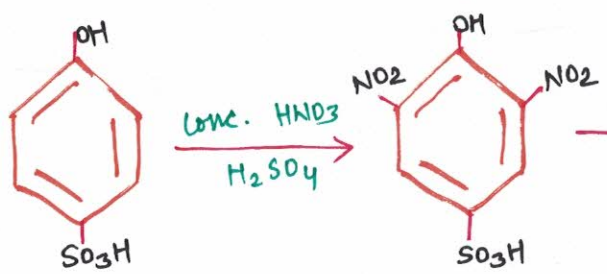
Picric acid



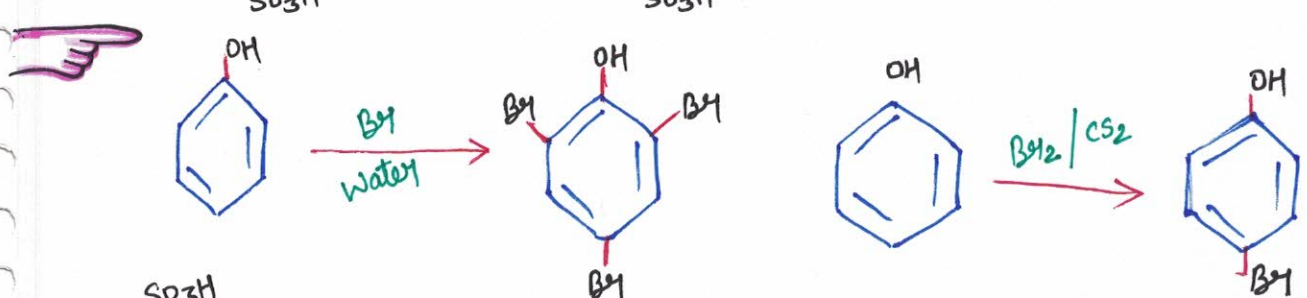
Picric acid

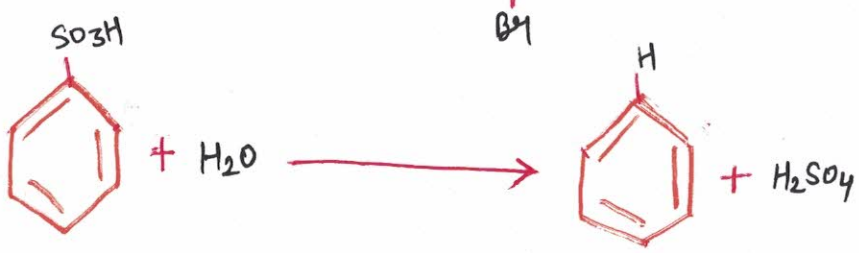


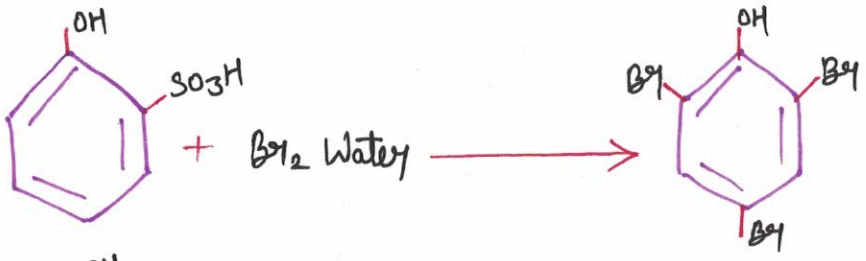
Picric acid

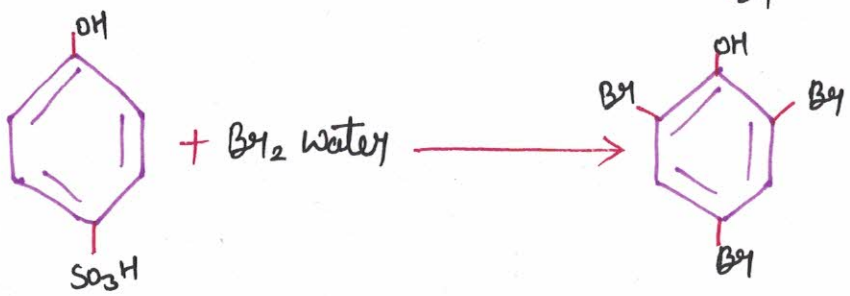


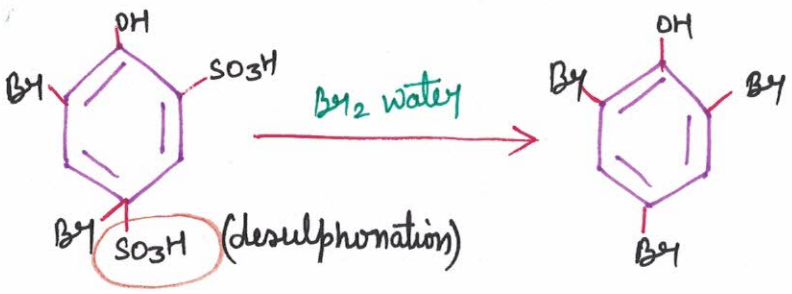
Picric acid

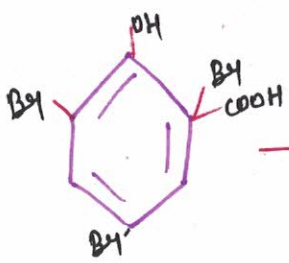


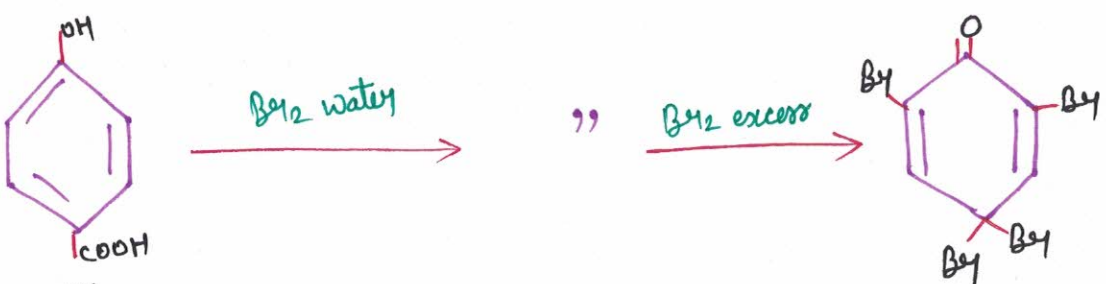


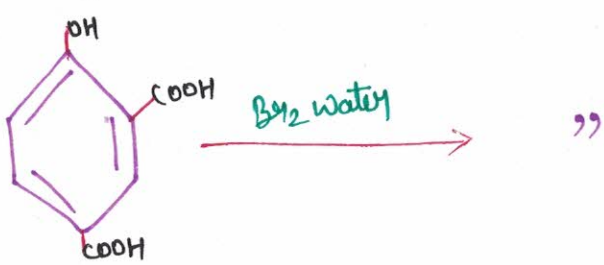


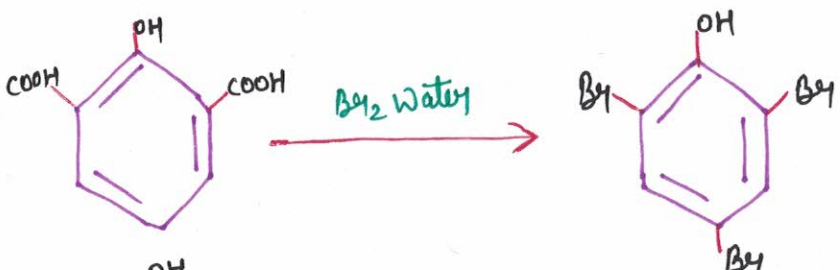


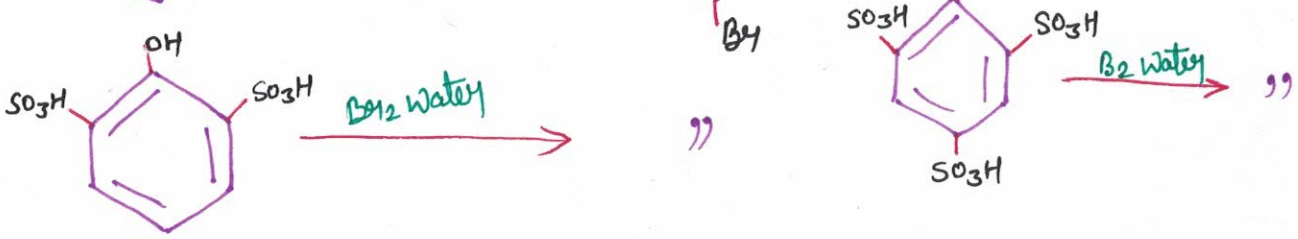


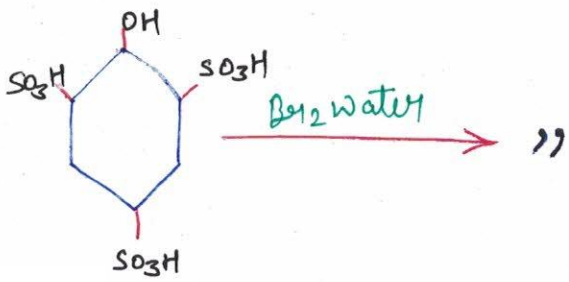


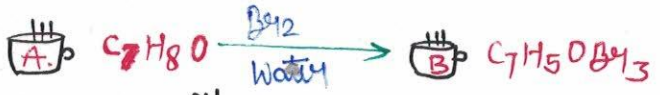




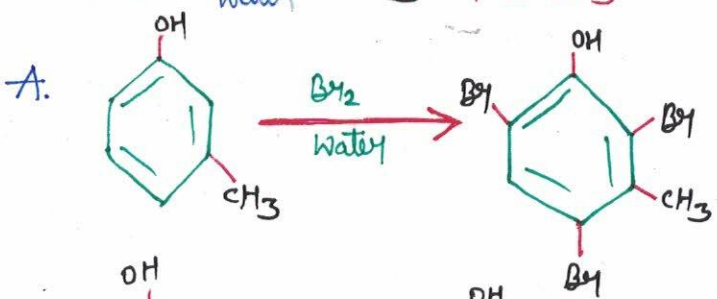


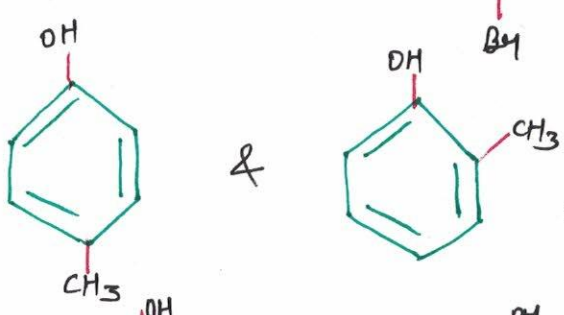




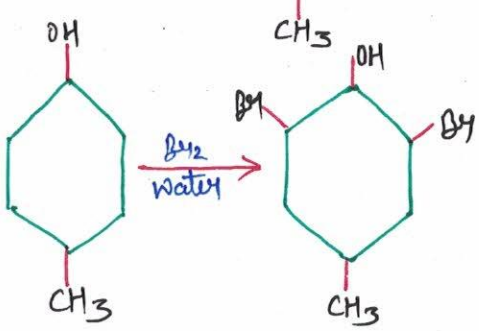


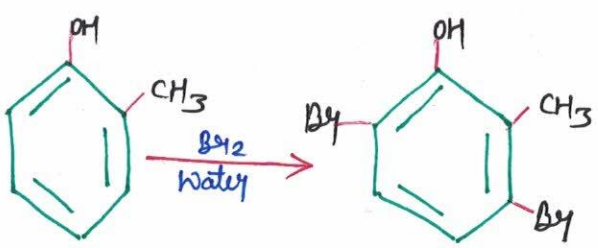
A.



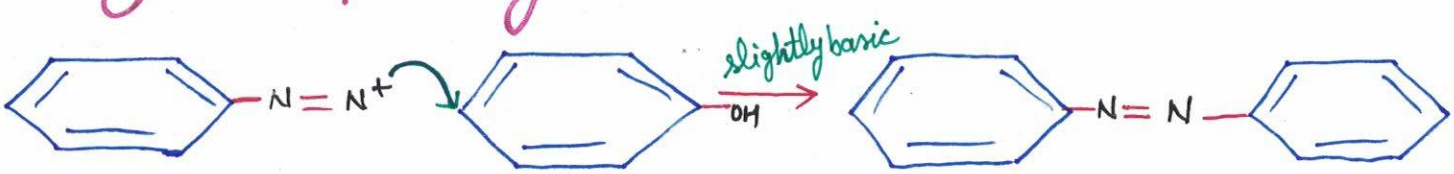


do not give tribromo derivative

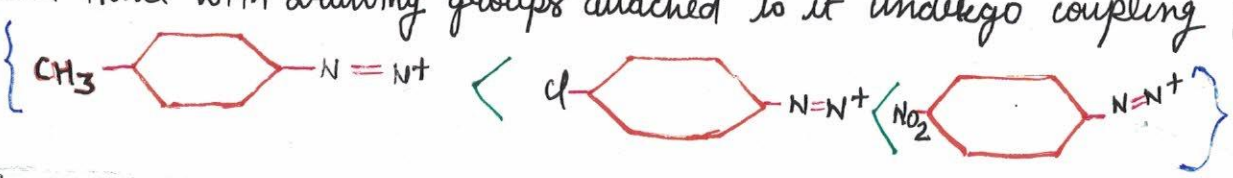




Azocoupling Reaction



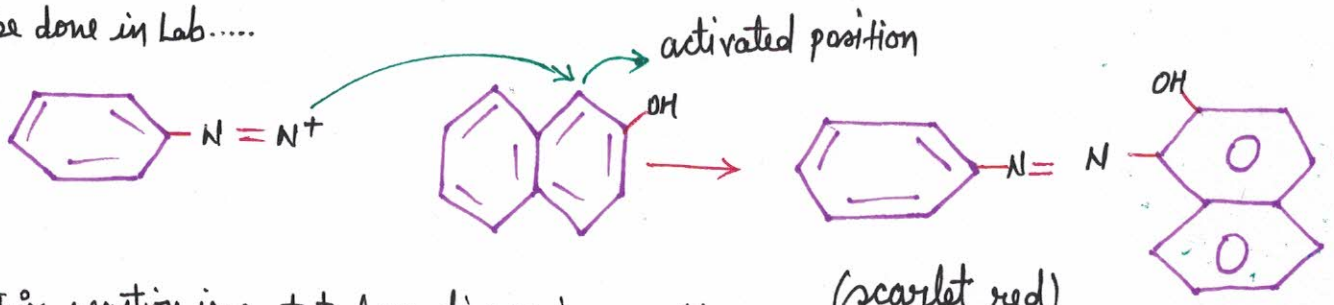
Diazobenzene is a reagent in this case not an intermediate so it should be unstable Hence with drawing groups attached to it undergo coupling fast.

Rate : 

Rings having high releasing groups can undergo this coupling like phenols and anilines.

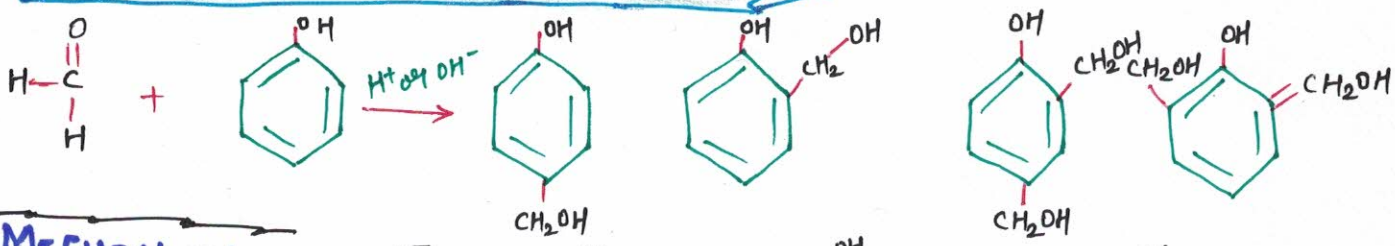
Diazobenzene salt is unstable over 0°C Hence strong releasing group attached ring should be used so that there is no need of heating to increase rate of reaction.

To be done in Lab.....

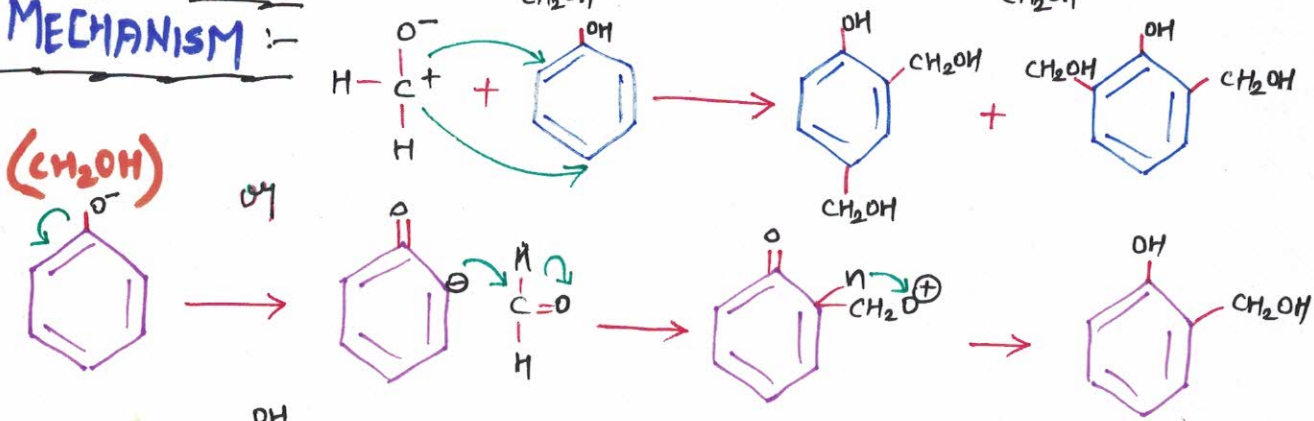


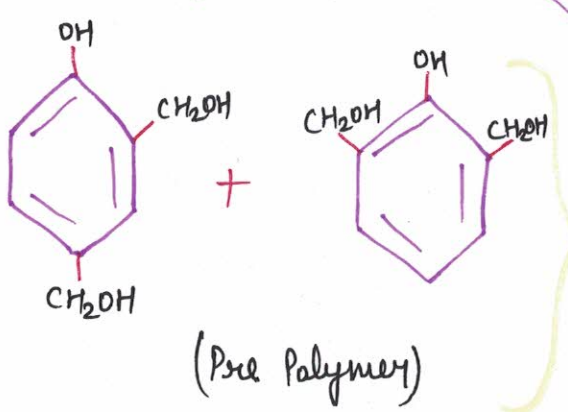
This reaction is a test for diazonium salt and β napthol. (scarlet red)

REACTION WITH FORMALDEHYDE



MECHANISM :-

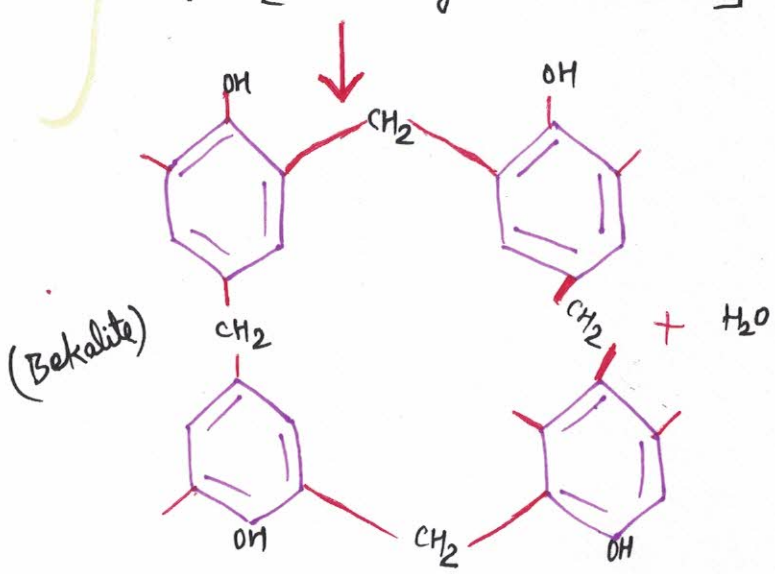




(Pre Polymer)

Hexamine $[(CH_2)_6N_4]$

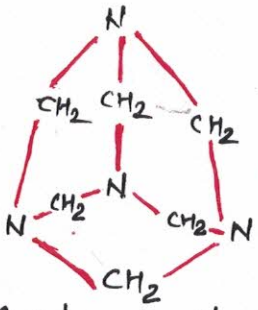
a curing agent a crosslinking agent [hexamethylene ultra amine].



(Bekalite)

Phenol formaldehyde is a thermoset polymer i.e once formed its shape cannot be changed. Thermoplastic polymer's shape can be changed. Water is formed as by product.

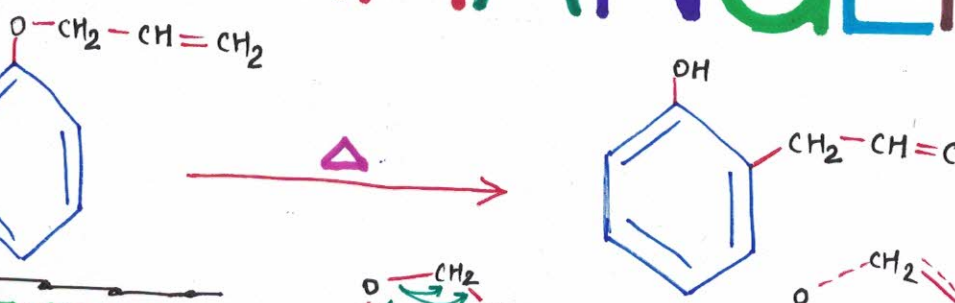
Hexamine can be prepared by $HCHO + NH_3 \xrightarrow{\Delta}$



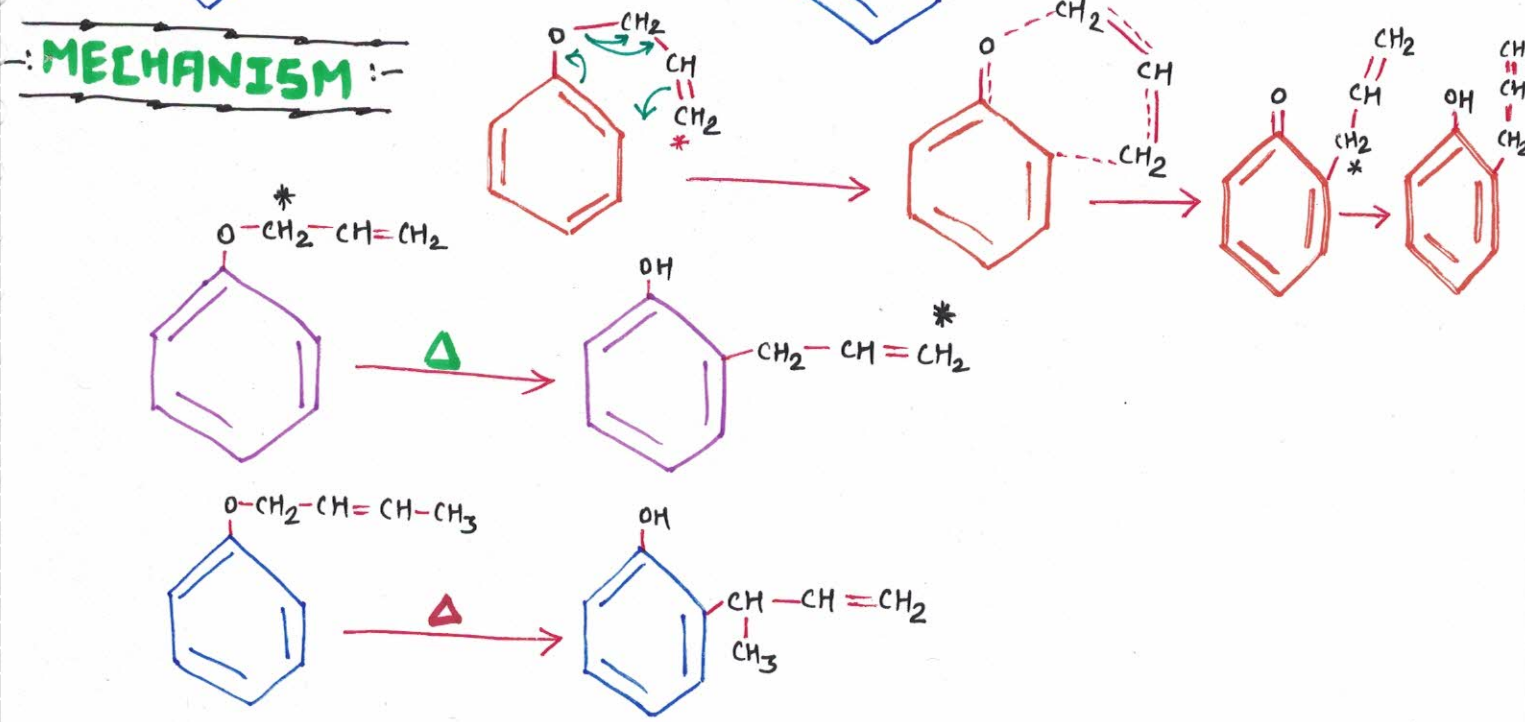
→ Hexamine

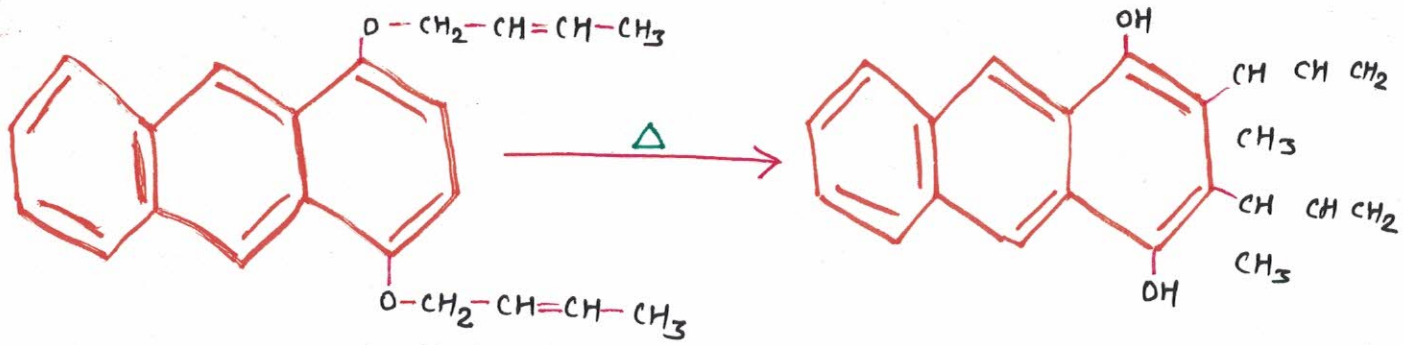
Bekalite is a condensation polymer, it cannot be melted and used in insulation purpose. Thermoplastics melt.

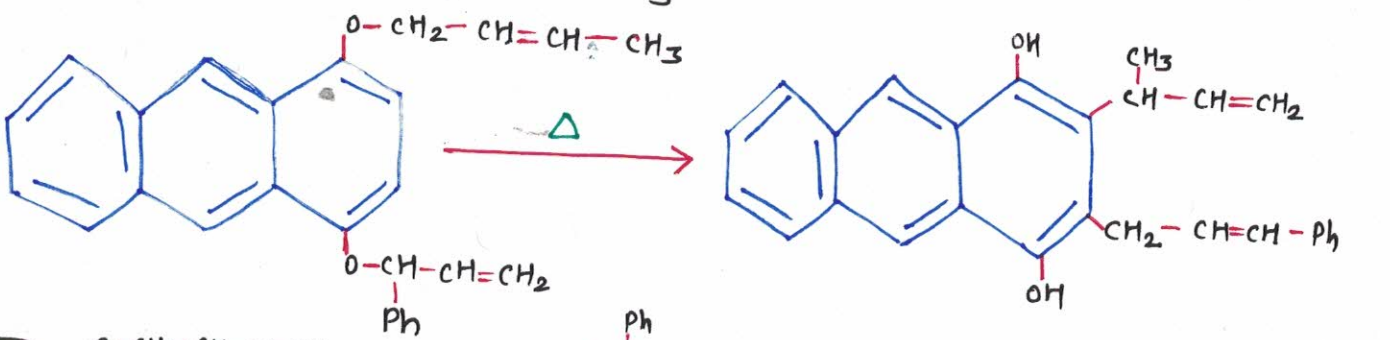
CLAISEN'S REARRANGEMENT

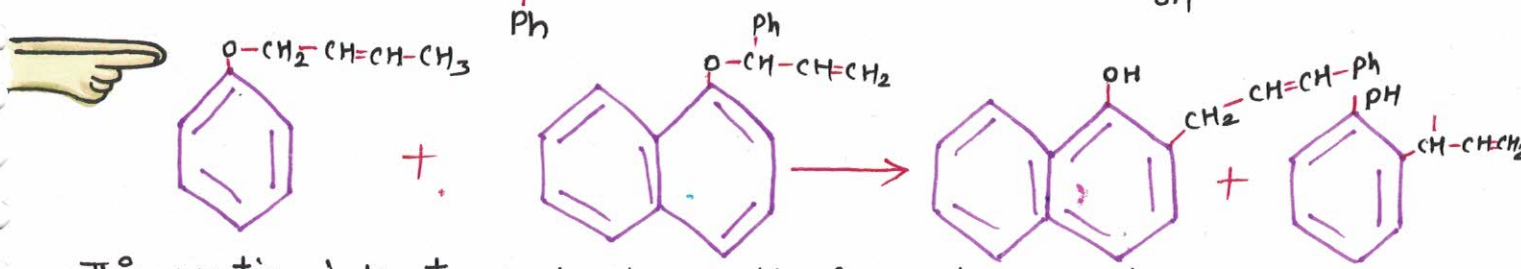


MECHANISM :-



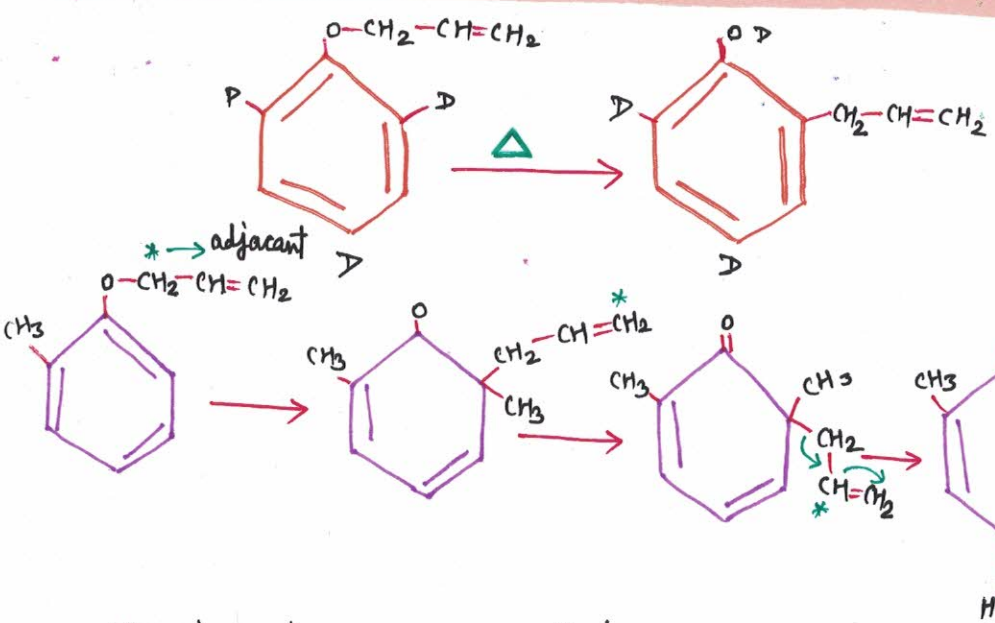






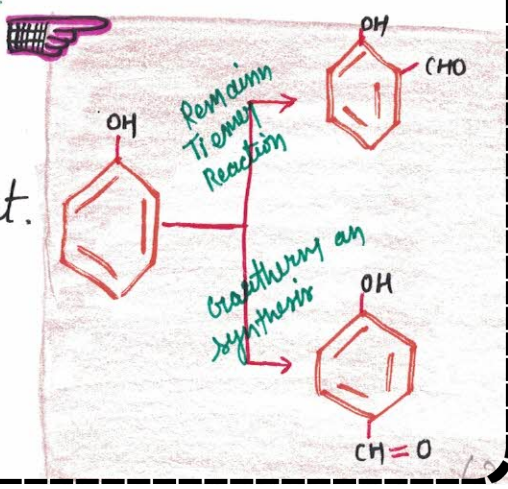
This reaction indicates that this reaction is a intramolecular reaction.

Hence, Claisen's rearrangement is an intramolecular reaction.



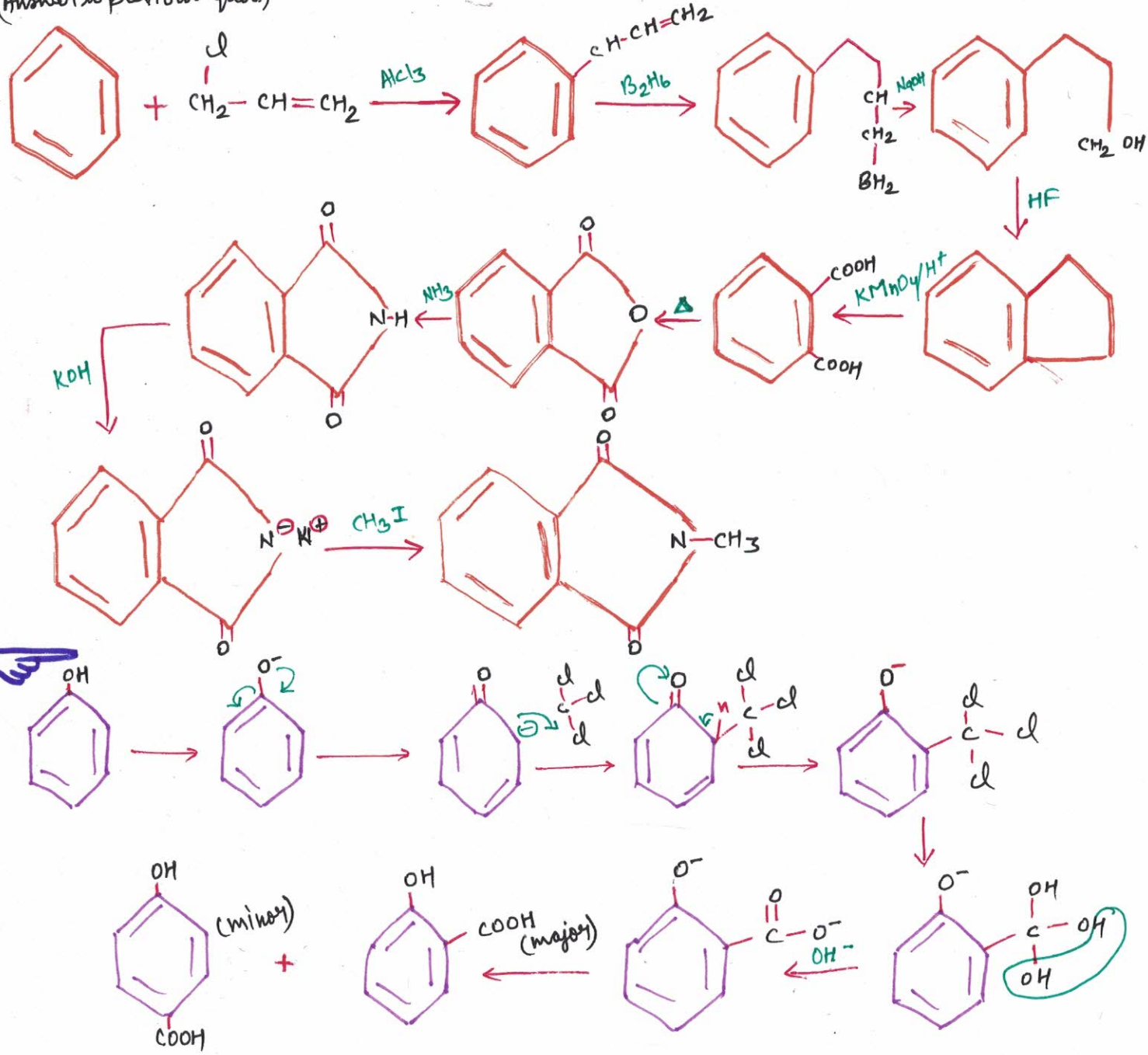
Two inversion → some labelled carbon
i.e terminal → terminal
adjacent → adjacent

Like in previous, e.g, adjacent still remains adjacent.



PRACTICE CLASS

(Answer to previous ques.)

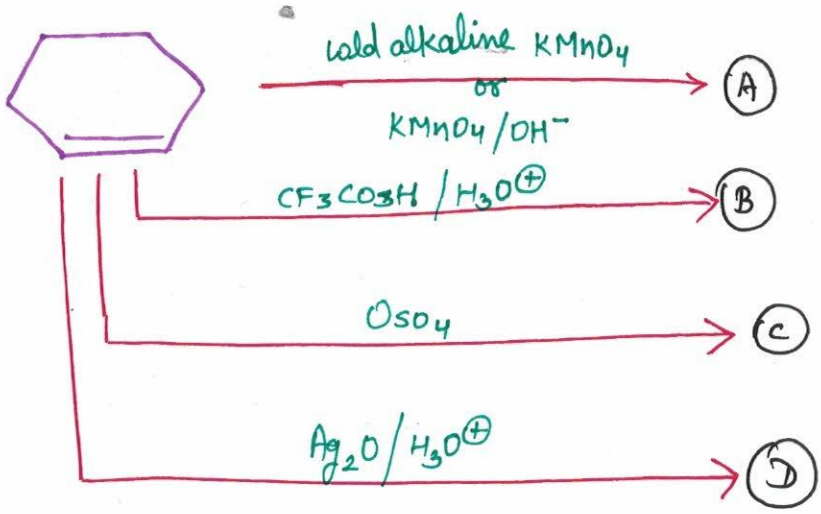


Some phenol reaction written later.

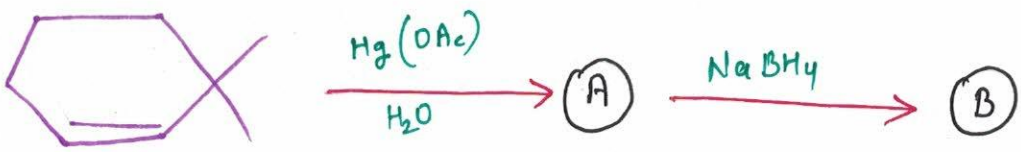
QUESTIONS ALCOHOLS AND PHENOLS

ALCOHOLS PHENOLS

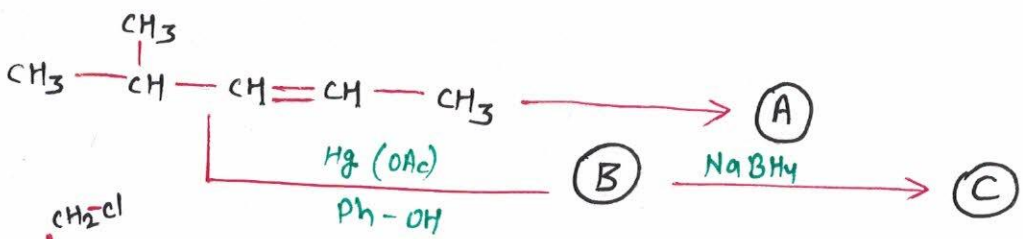
Q. 1.



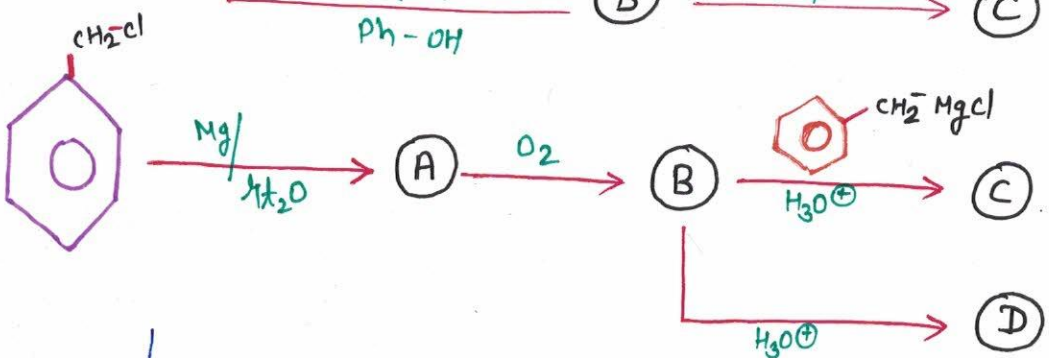
Q. 2.



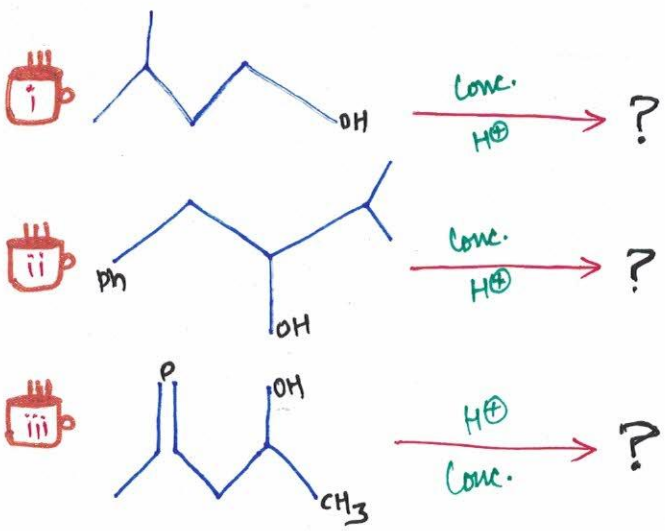
Q. 3.



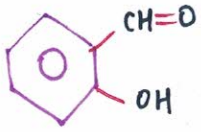
Q. 4.

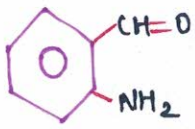


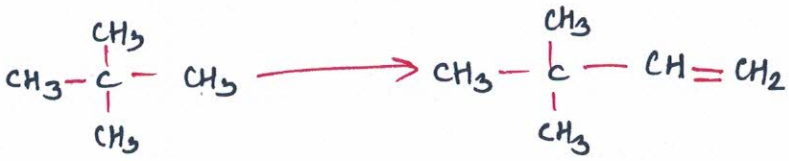
Q. 5.

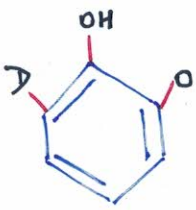


6.  $\xrightarrow[+\ NaOH]{K_2S_2O_8}$ (A) $\xrightarrow{H_3O^+}$ (B)

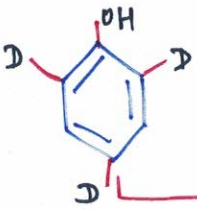
7. i  (i) H_2O_2 NaOH (ii) H_3O^+ → (A)

ii  (i) H_2O_2 + NaOH (ii) H_3O^+ → (B)

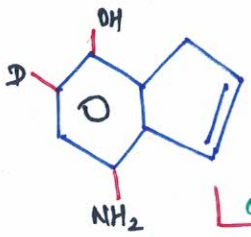
8. Convert 

9.  (i) NaOH (ii) CO_2 (iii) H^+ → (A)

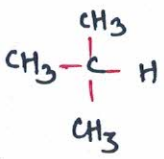
(i) NaOH (ii) CO_2 (iii) D^+ → (B)

10.  $\xrightarrow[alc\ KOH]{CHCl\ BrI}$ (A)

$\xrightarrow[KOH]{CBr_2I_2}$ (B)

 $\xrightarrow[t\text{-}BuO^-]{CHCl\ BrI}$ (C)

$\xrightarrow[H_3O^+]{CCl_2BrI + OH^-}$ (D)

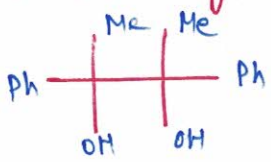
11.  $\xrightarrow{X_2}$ (A) $\xrightarrow{Mg/dry\ ether}$ (B) $\xrightarrow{CH_2-O-CH_2}$ (C) $\xrightarrow{H_3O^+}$ (D) $\xrightarrow{Al_2O_3}$ (E)

12. Find no. of substitution and additions.

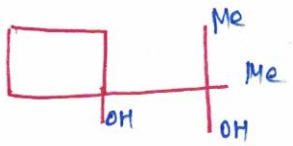
(a) $CH_3-MgX + COCl_2 \longrightarrow ?$

(b) $CH_3-MgX + Et-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow ?$

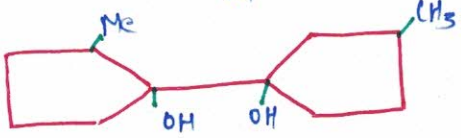
13. React each undergiven with ($\xrightarrow[H_2O]{Mg/Hg}$), i.e (Pinacol - Pinacolone).

a. 

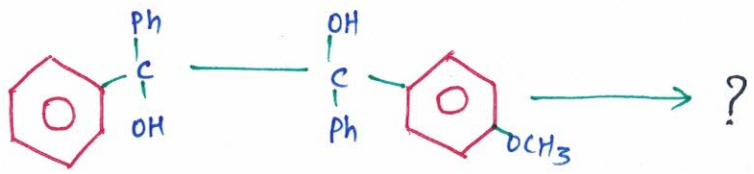
?

b. 

?

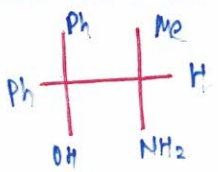
c. 

?

d. 

?

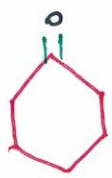
14. Complete the γXH.

a. 

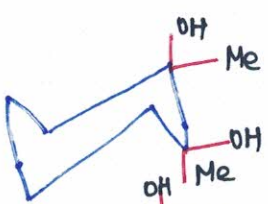
$\xrightarrow{HNO_2}$ (B) $\xrightarrow{-H^+}$ (C)

b. 

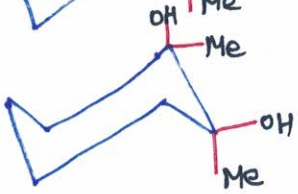
$\xrightarrow[dil\ O^-]{CH_3NO_2}$ (A) $\xrightarrow{LAH}$ (D) $\xrightarrow[H^+]{HNO_2}$ (E)

c. 

$\xrightarrow[(ii)\ H_3O^+]{(i)\ Mg/Hg}$ (F) $\xrightarrow{H_2SO_4}$ (G)

15. a. 

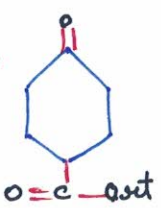
$\xrightarrow{H^+}$ (B)

b. 

$\xrightarrow{H^+}$ (C)

16. a. 

$\xrightarrow[H_3O^+]{LiAlH_4}$ (A)

b. 

$\xrightarrow[H_3O^+]{NaBH_4}$ (A)

$\xrightarrow[H_3O^+]{LiAlH_4}$ (B)

17.

a. $CH_3-CH=CH_3 \xrightarrow[CH_3OH]{Hg(OAc)_2} (A) \xrightarrow{NaBH_4} (B)$

b.  $+ C_2H_5I \xrightarrow[Anhyd\ (C_2H_5OH)]{C_2H_5O^-} (C)$

c.  $+ C_2H_5I \xrightarrow[Anhyd\ (CH_3OH)]{CH_3O^-} (D)$

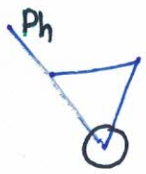
d.  $+ PhOH \xrightarrow[Anhyd\ (2°-OH)]{C_2H_5O^-} (E)$

e. $HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-{}^{18}OH + H-O-CH_2-CH_2-OH \xrightarrow{H^+} (F)$

f. Which is faster? (Acylation or esterification)

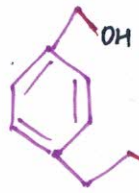
g. $CH_3-\underset{CH_3}{CH}-\underset{OH}{CH}-CH_3 \xrightarrow[H^+]{KMnO_4} ?$ Many times

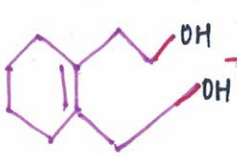
h. $CH_3-CH=CH_3 \xrightarrow{NBS} (A) \xrightarrow{Br_4} (B) \xrightarrow[KOH]{Alc} (C)$

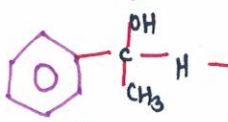
i.  $\xrightarrow[(ii)\ SnCl_2+HCl]{(i)\ Aq.\ AgCN} ?$

$\xrightarrow{(i)\ NH_3} ?$

18.

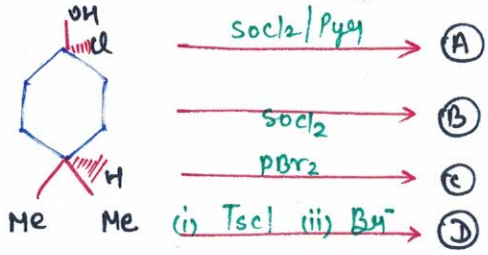
(i)  $\xrightarrow{MnO_2} (A)$

(iii)  $\xrightarrow{MnO_2} (B)$

(iii)  $\xrightarrow[\Delta]{Cu} (C)$

(iv) $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[\Delta]{Cu} (D)$

19. Give stereochemical products.



20. (i)

Conc. H_2SO_4, 80°C → A

Conc. H_2SO_4, 160°C → B

A, B → C, A

(ii)

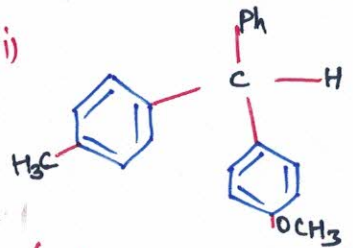
Br_2/Fe → B; (i) Sn/HCl (iii) HNO_2 → C; H_2O → D

21. (i)

+ $CH_3-CH=CH_2$, H^+ → A; O_2 → B; H_2SO_4, Δ → C + D

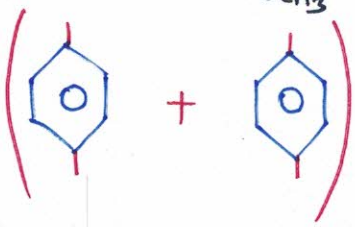
(This reaction is used for the preparation of Phenols).

(ii)



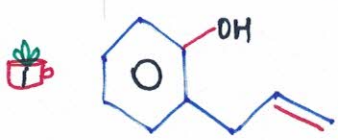
O_2 → A; Δ, H^+ → B + C

(iii)

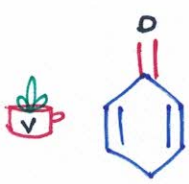


$NaHCO_3$ → what will be the residue ? why ?

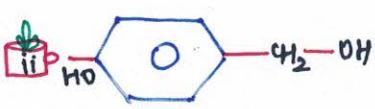
22.



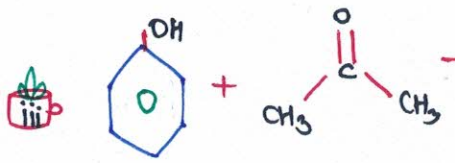
(i) CH_3CO_3H (iii) H_3O^+ → A



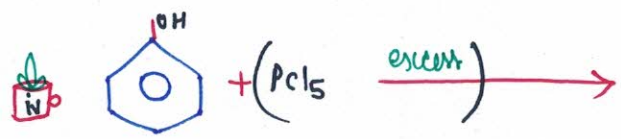
$\overline{OH}$, H_2O → C



$SOCl_2$ → B

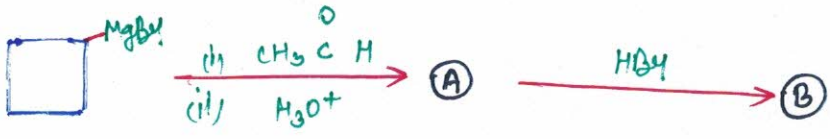


HCl → D

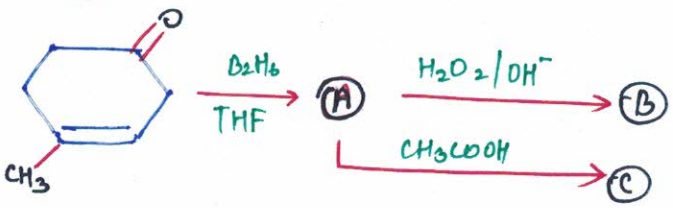


+ (PCl_5, excess) →

23.

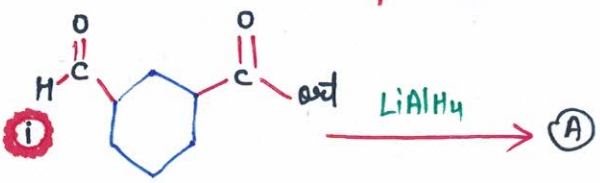
(i) 

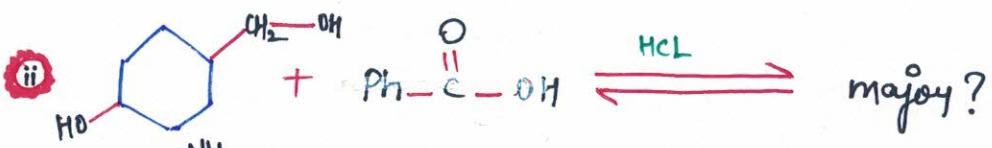
(ii) 

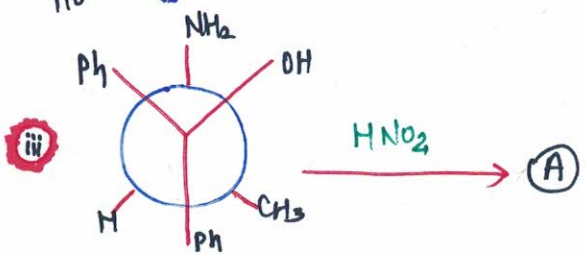
(iii) 

24. convert Phenol to aspirin.

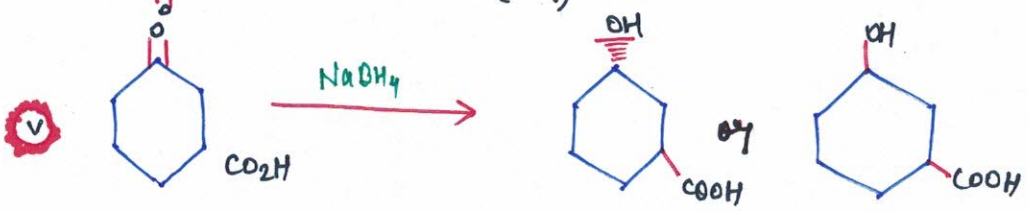
25.

(i) 

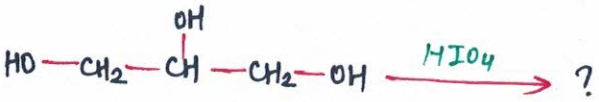
(ii) 

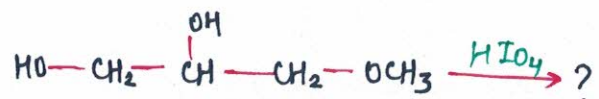
(iii) 

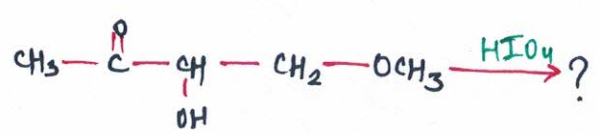
(iv) 

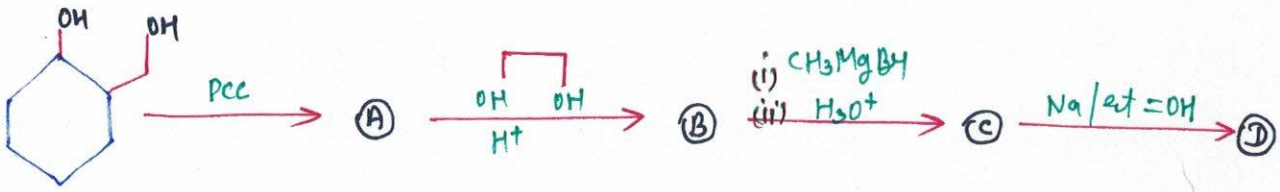
(v) 

26.

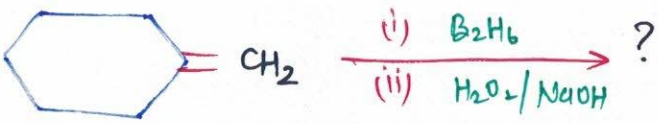
(i) 

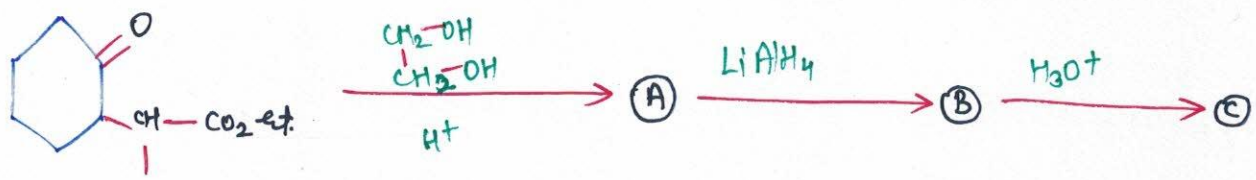
(ii) 

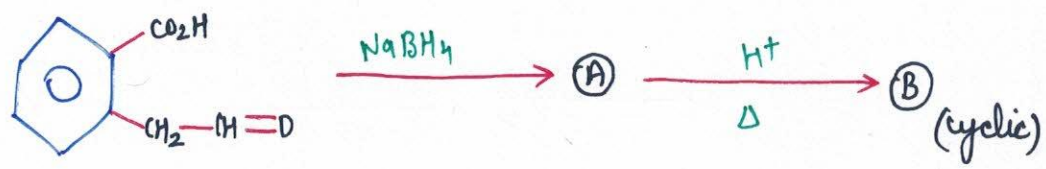
(iii) 

27. 

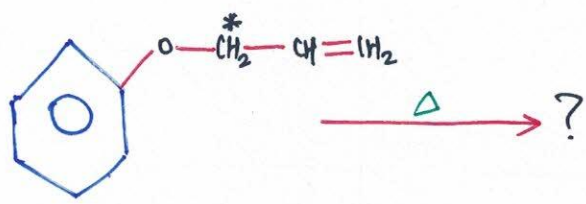
28. (i) 

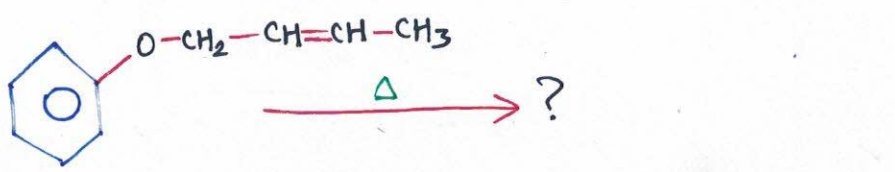
(ii) 

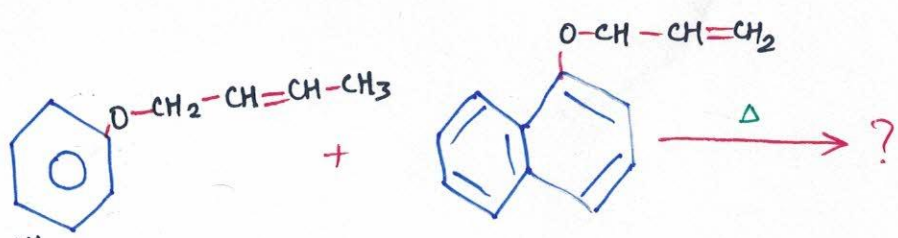
(iii) 

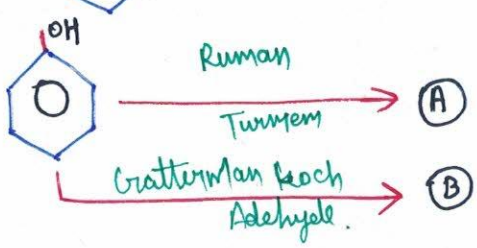
(iv) 

(v) 

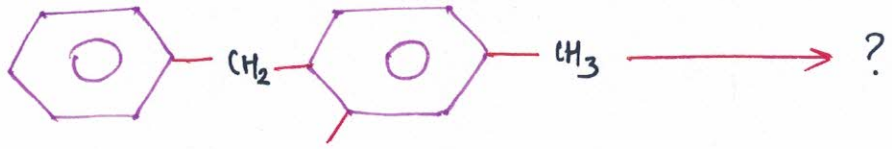
(vi) 

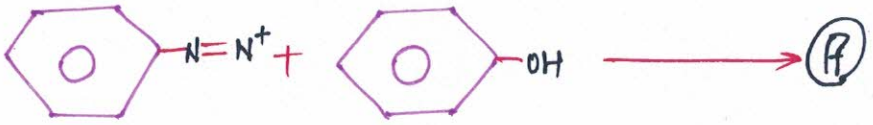
29. (i) 

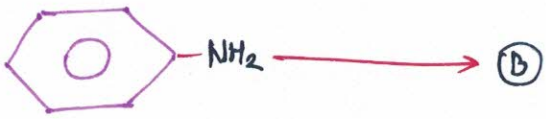
(ii) 

30. 

31. Q.

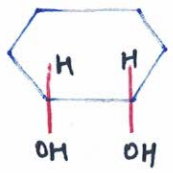
(i) 

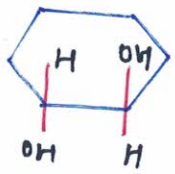
(ii) 

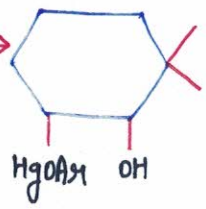
" +  → (b)

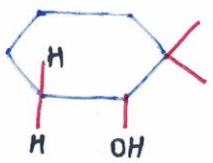
" +  → (c)

SOLUTION OF ALCOHOLS PHENOLS

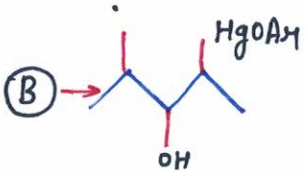
ANS. 1. (A), (C) → 

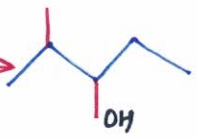
(B), (D) → 

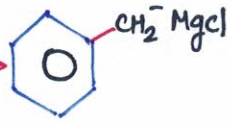
ANS. 2. (A) → 

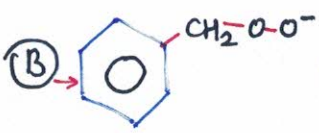
(B) → 

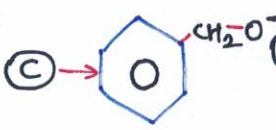
ANS 3 (A) → 

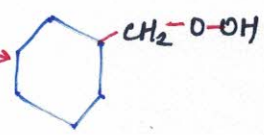
(B) → 

(C) → 

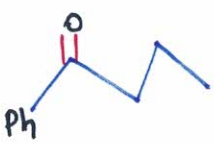
ANS. 4 (A) → 

(B) → 

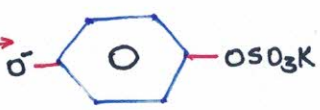
(C) → 

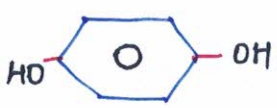
(D) → 

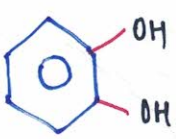
ANS 5 (i) → 

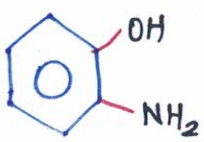
(ii) 

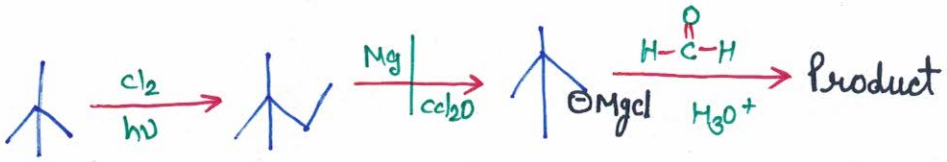
(iii) 

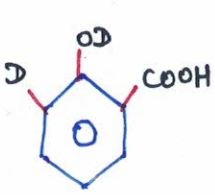
ANS. 6 (A) → 

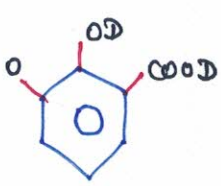
(B) → 

ANS. 7 (A) → 

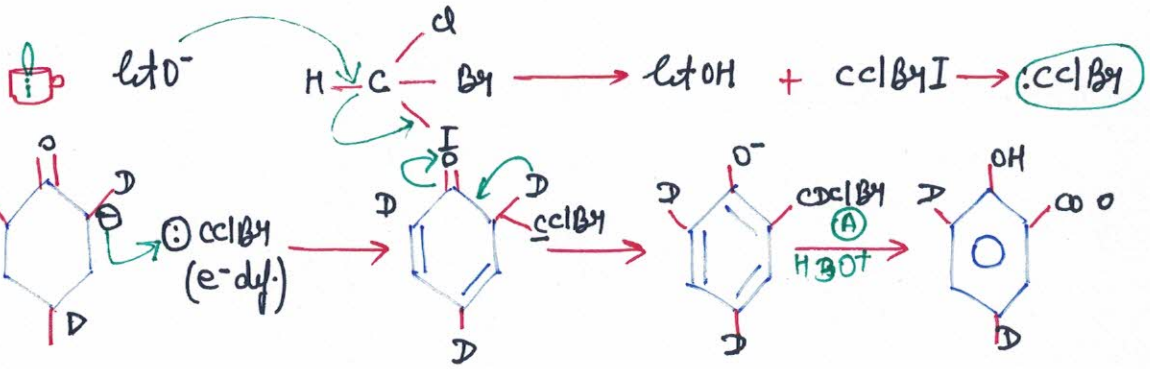
(B) → 

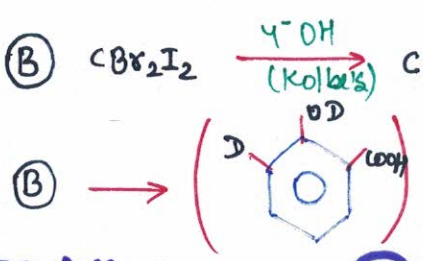
ANS. 8. 

ANS. 9. (A.) 

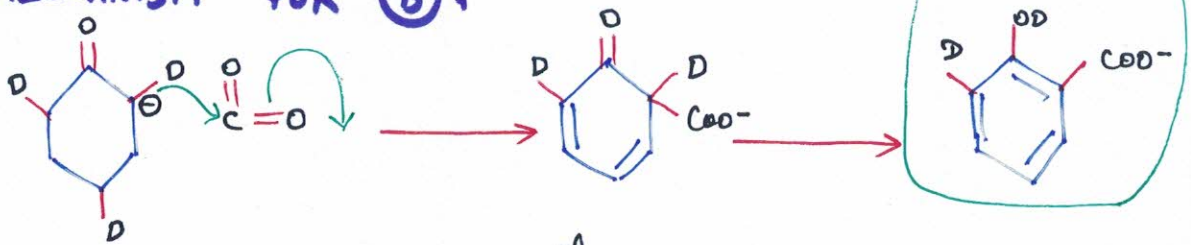
(B) 

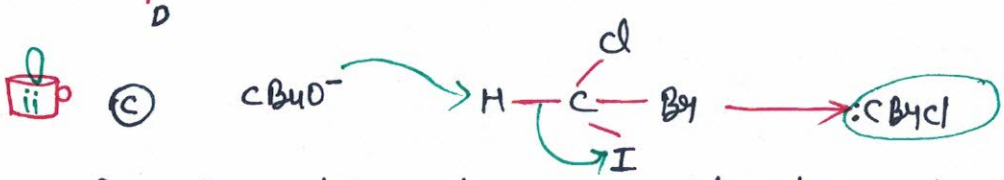
ANS. 10.



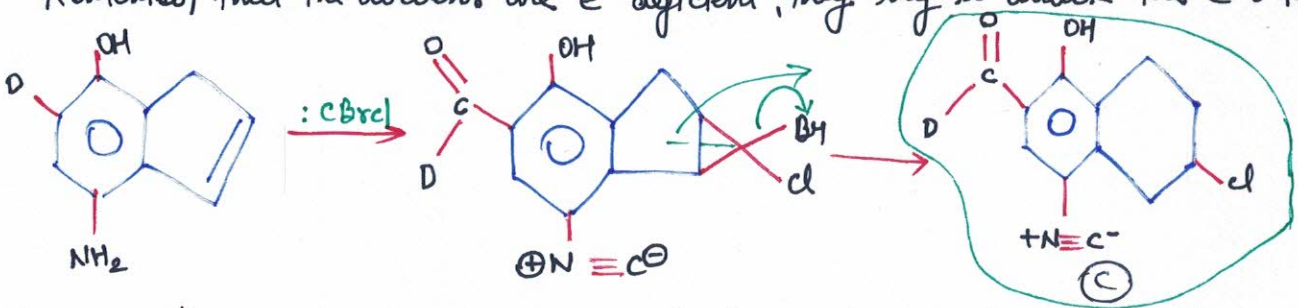


MECHANISM FOR (B) ;

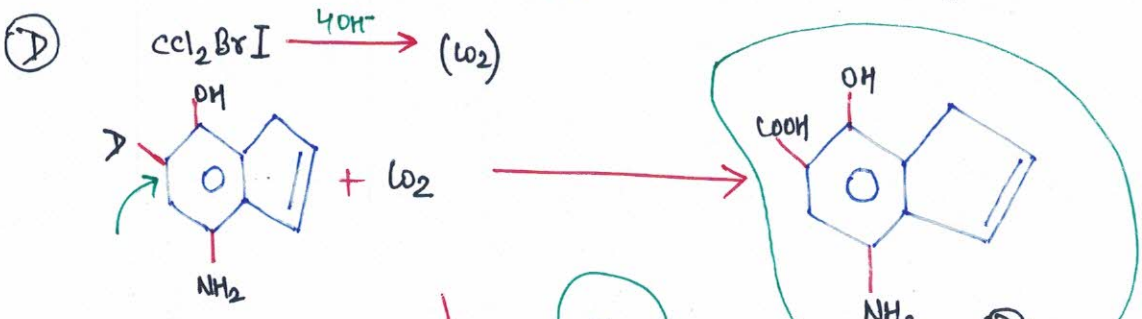




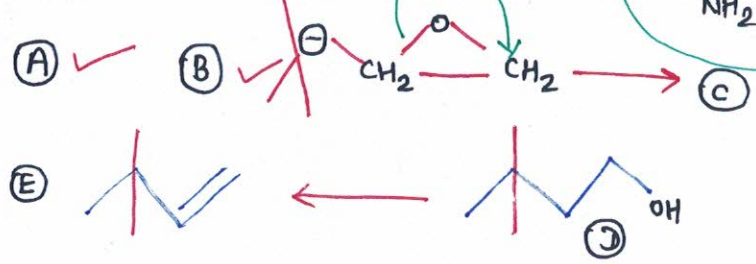
Remember that the carbene are e⁻ deficient, they try to attack the e⁻ rich.



carbene converts $-NH_2$ to $-N^{+}\equiv C^{\ominus}$ and also undergoes Reimann Teimenn rxn.

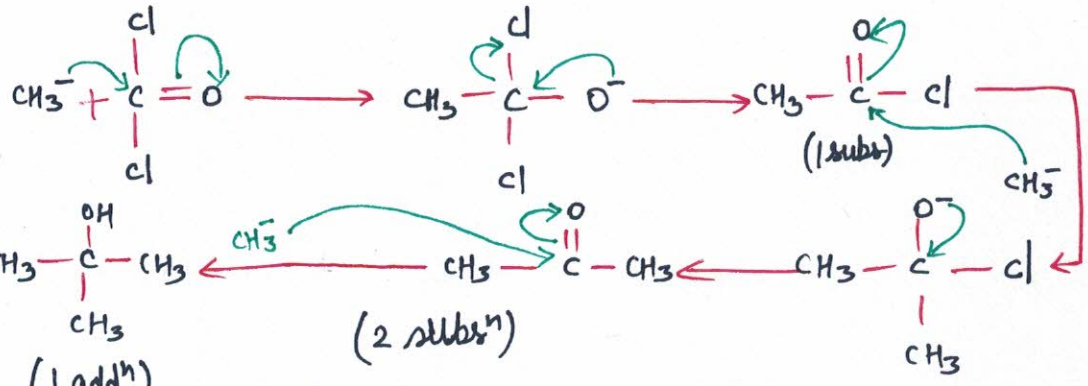


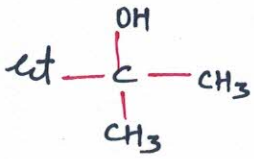
ANS 11.



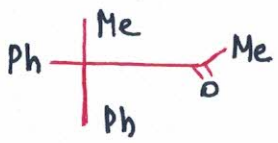
ANS. 12.

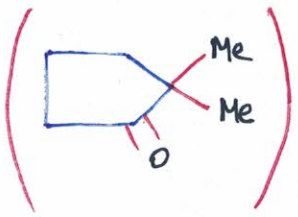
a.

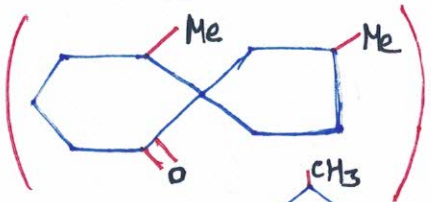


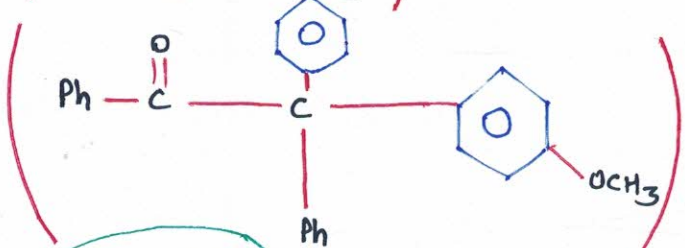
b. final prod →  (1 subsⁿ + 1 addⁿ)

ANS 13.

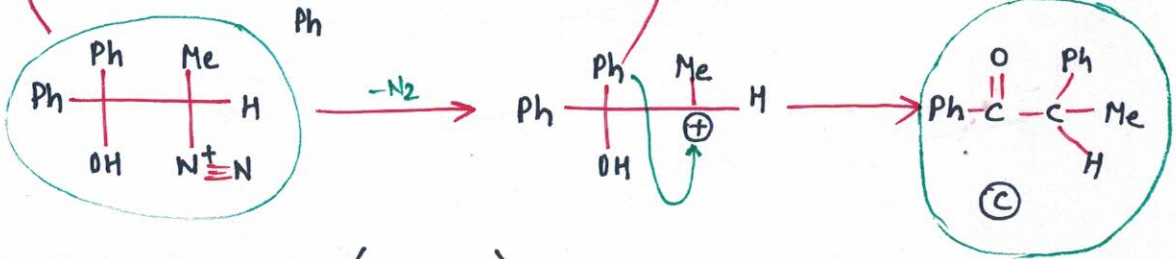
a. 

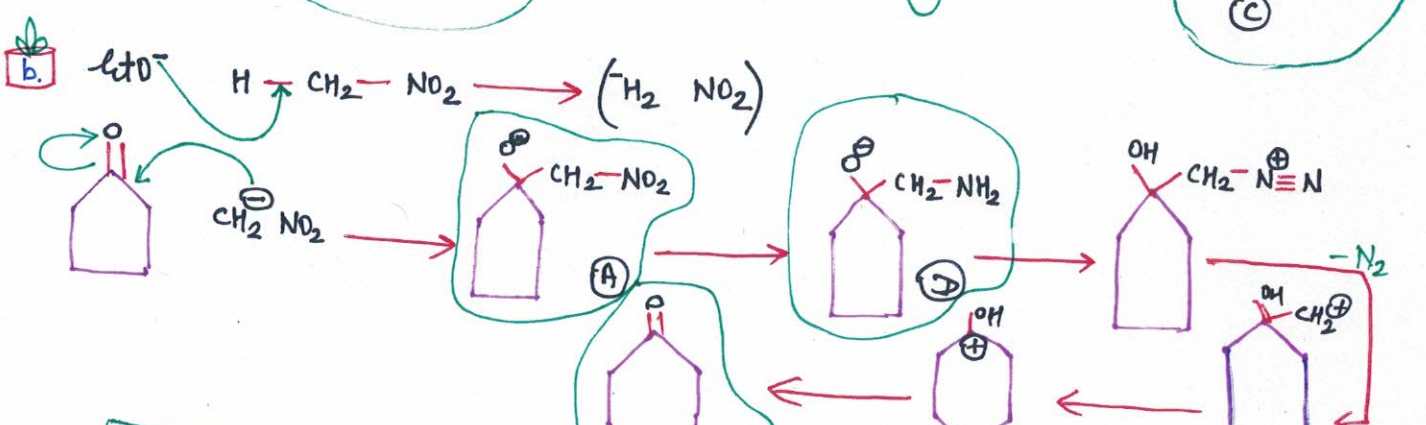
b. 

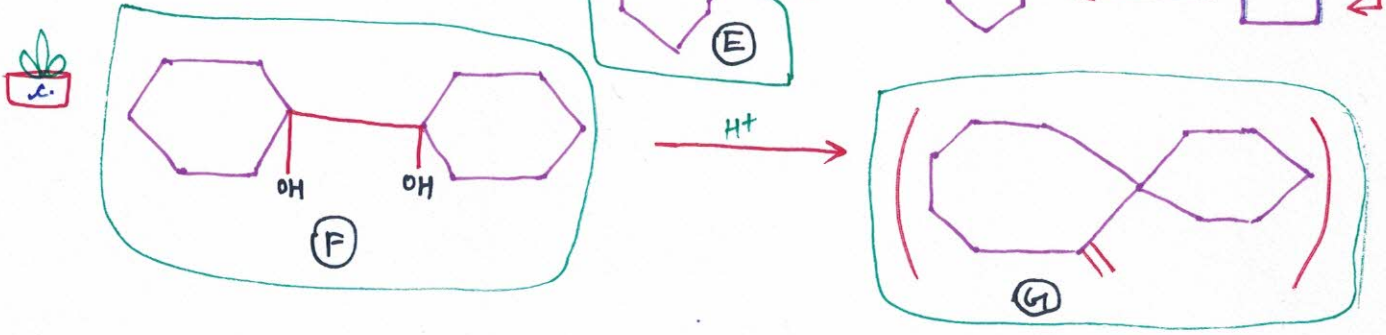
c. 

d. 

ANS. 14.

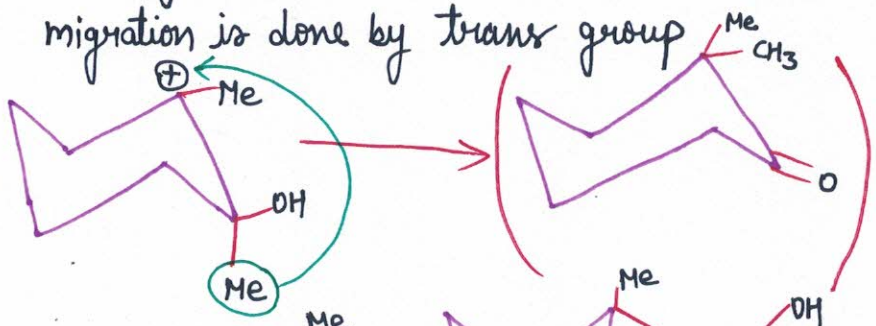
a. 

b. 

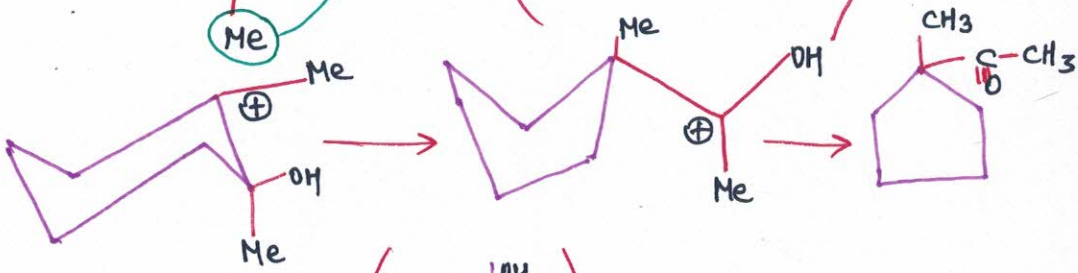
c. 

ANS. 15. As dehydration is a trans mechanism, then the carbocation migration is done by trans group

a.

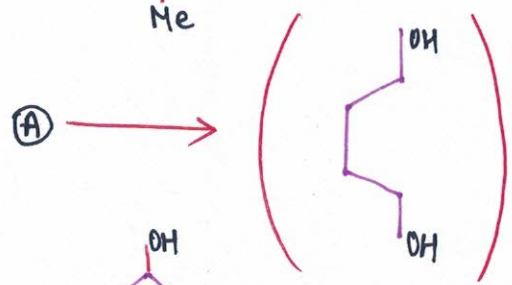


b.

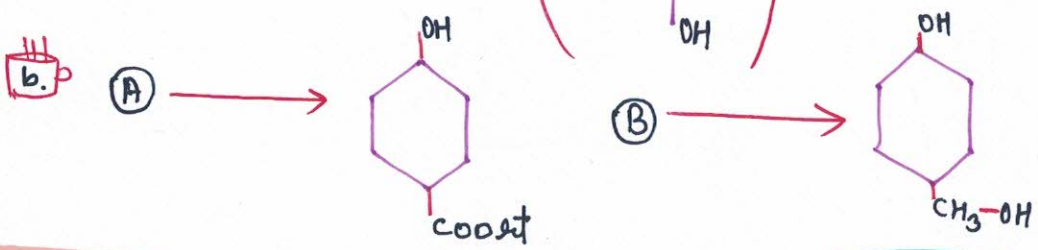


ANS. 16.

a.

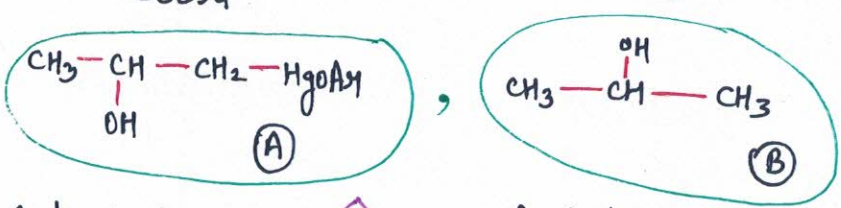


b.



ANS. 17.

a.

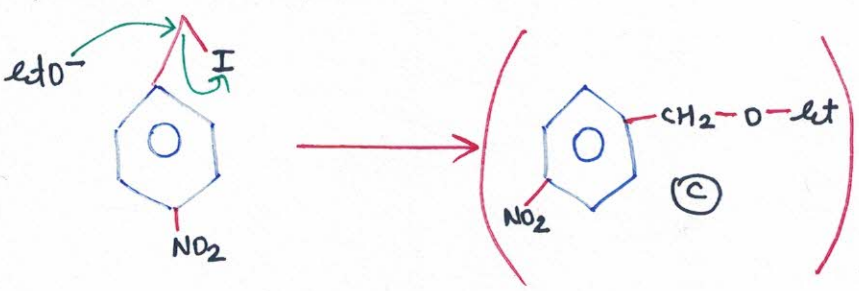


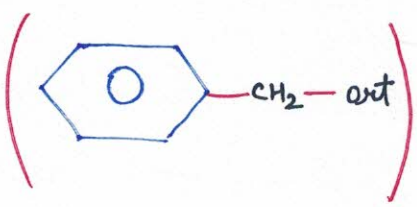
b. $C_2H_5O^-$ is a base thus,  Basicity of $EtO^- > Ph\text{-}O^-$

$\therefore EtO^-$  C

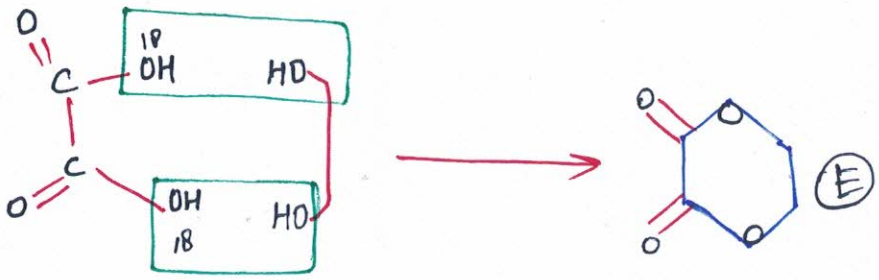
c. $C_2H_5O^-$ takes Ph OH and becomes Ph O^- (NO_2) As basicity of $C_2H_5O^-$ Ph O^- (NO_2)

thus, EtO^- attacks



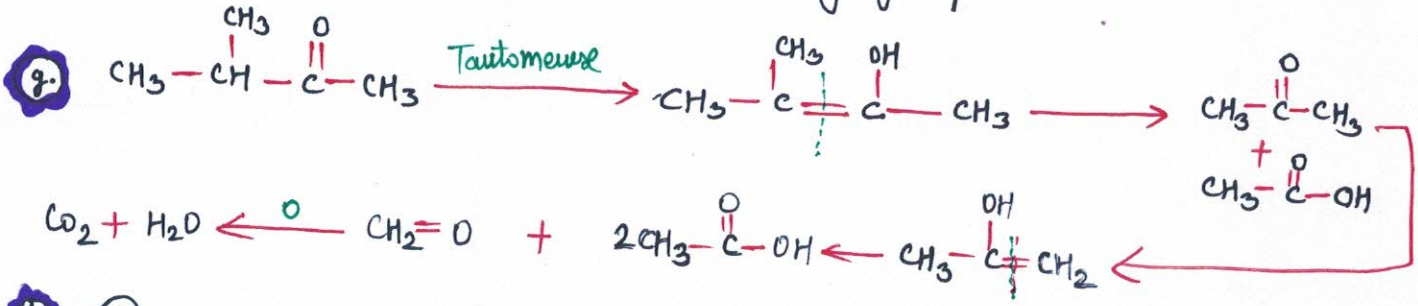
d.  D

e.

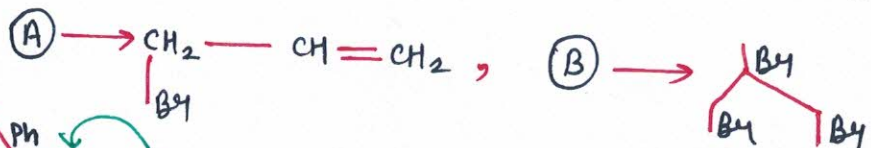


f. Acylation is faster as Cl^- is better leaving group.

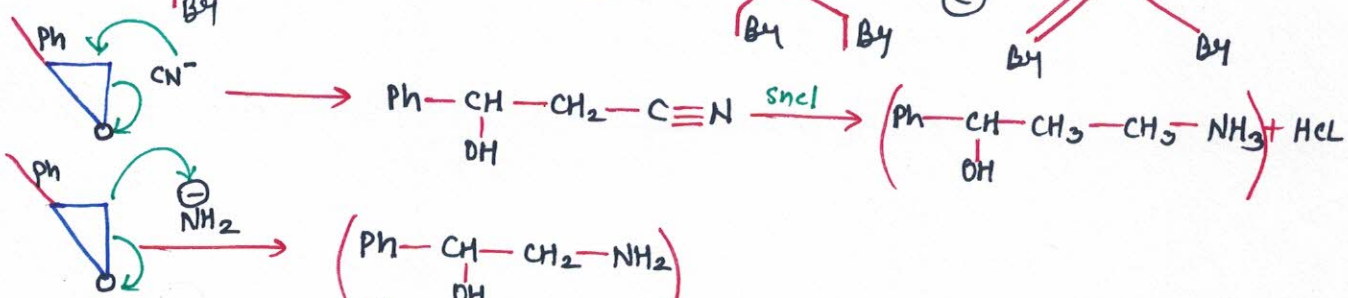
g.



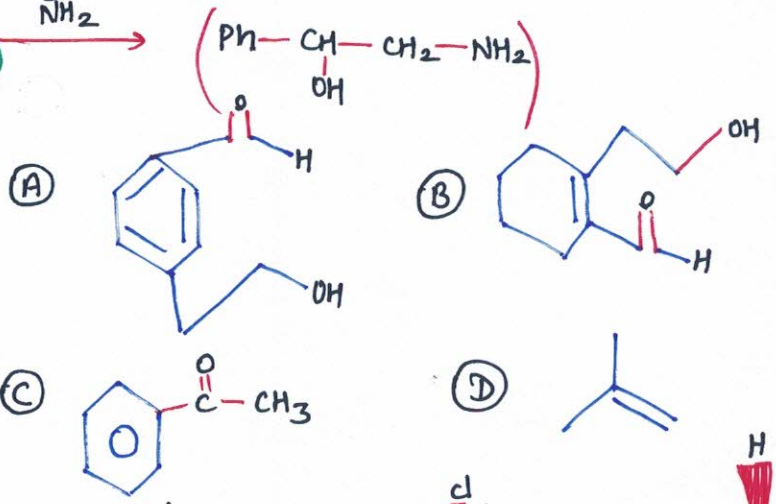
h.



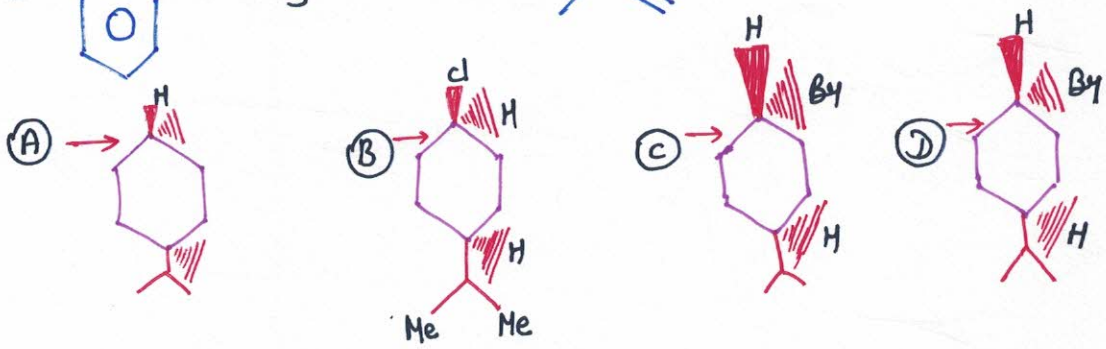
i.



ANS. 18.

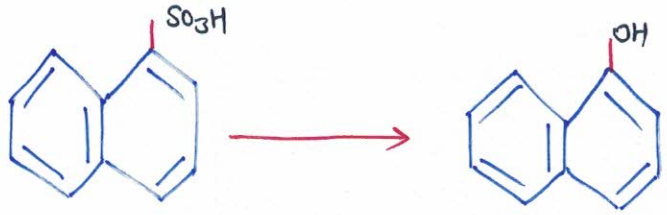


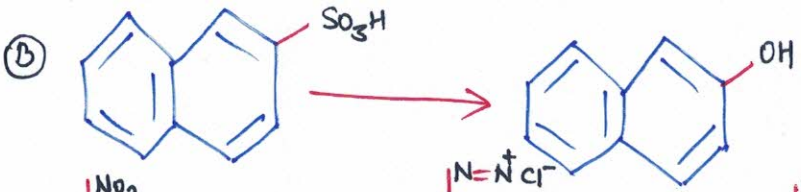
ANS. 19.

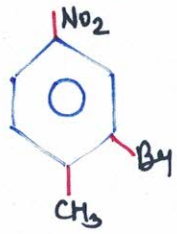


R-OH with $SOCl_2$ gives R-Cl (with retention of configuration). but with SOCl/Pyr, RCl is formed with inversion of configuration (SN' reaction)

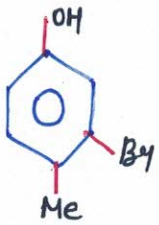
ANS. 20.

(i) (A) 

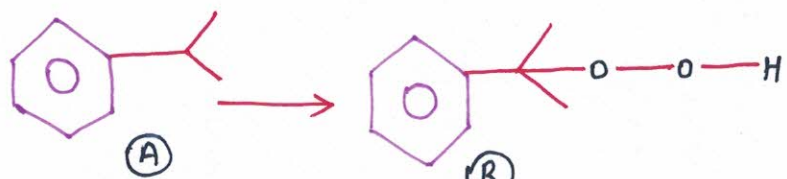
(ii) (B) 

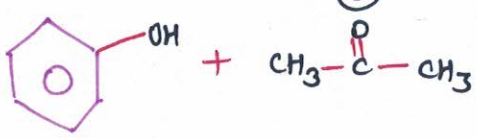
(B) 

(C) 

(D) 

ANS 21.

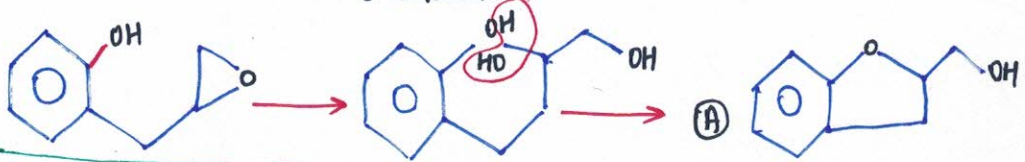
(i) 

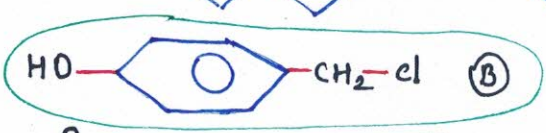
(C) + (D) = 

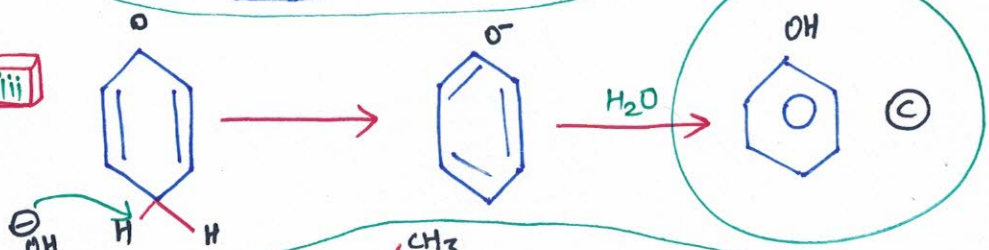
(ii) 

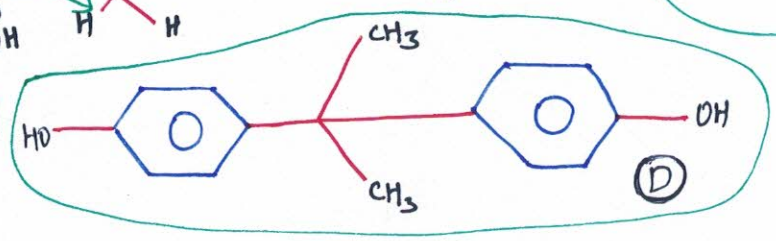
(iii) Acid reacts, thus, phenol derivation is the residue.

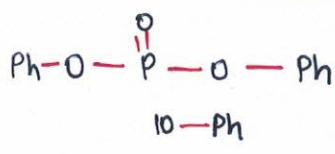
ANS. 22.

(i) 

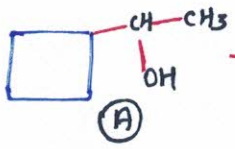
(ii) 

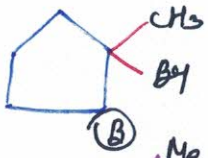
(iii) 

(iv) 

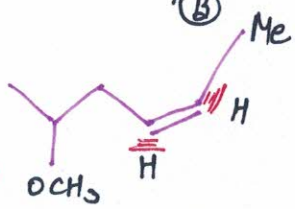
(v) 

ANS. 23. (i) (A)

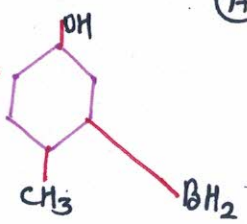


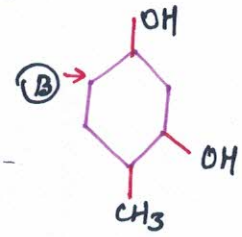


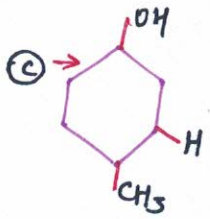
(ii) $CH_3-CH(OH)-CH_2-C\equiv C-CH_3$ (A)



(iii) (A)

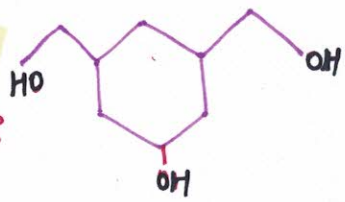


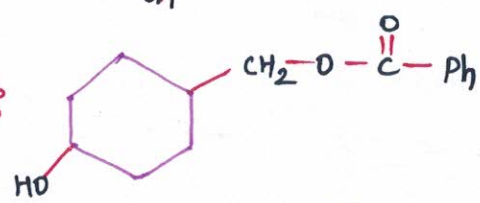


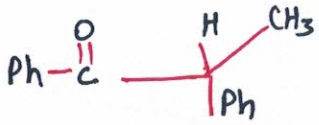


ANS. 24. Self...

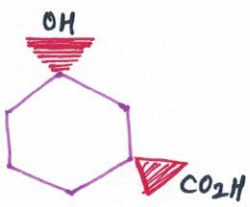
ANS. 25. (i)



(ii) 

(iii) 

(iv) x = 3

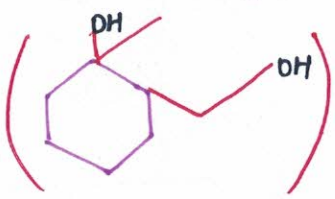
(v) 

ANS 26. (i) $2H-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-OH$

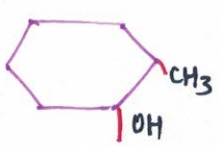
(ii) $2H-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-OH + CH_3-OH$

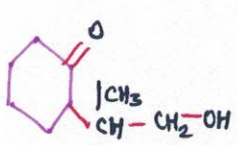
(iii) $CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3O-CH_2-\overset{O}{\overset{\|}{C}}-H$

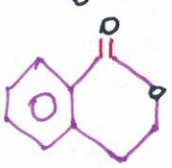
ANS. 27. (D) is



ANS. 28. (i) easy 

(ii) 

(iii) (C) is 

(iv) (B) is 

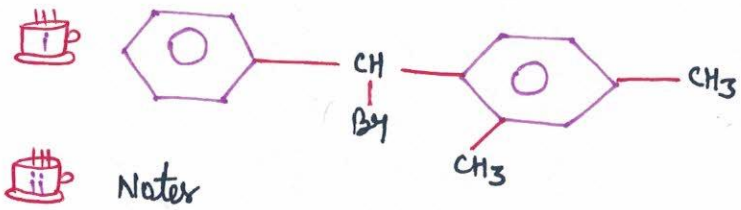
(v) easy

(vi) Mates

ANS 29. Notes

ANS 30 Notes

ANS 31.



(ii) Notes