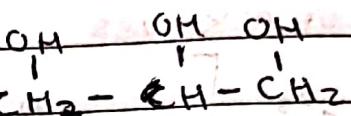


ALCOHOLS, PHENOLS AND ETHERS

NOMENCLATURE

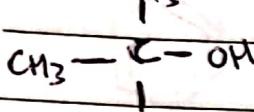
(i) Alcohols: $\text{CH}_3 - \text{CH}_2 - \text{OH}$

Ethanol



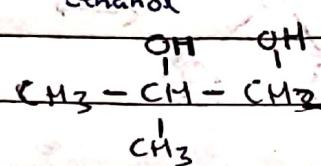
Propane-1,2,3-triol

Glycerol

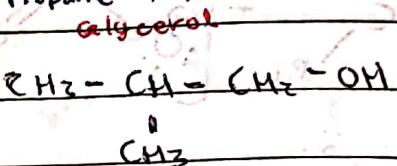


2-Methyl propan-2-ol

Isobutyl alcohol

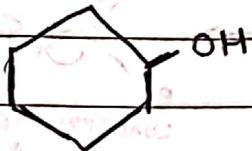


2-Methyl-propane-1,2-diol

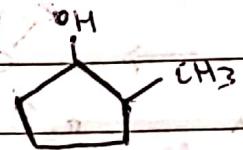


2-Methyl propan-1-ol

Isobutyl alcohol



Cyclohexanol

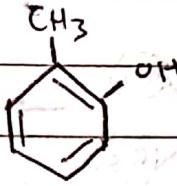


2-Methylcyclopentan-1-ol

(ii) Phenols:

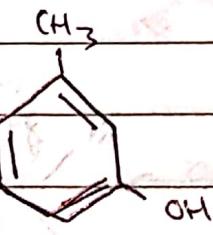


Phenol



2-Methylphenol

o-cresol



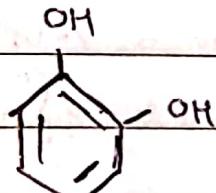
3-Methylphenol

m-cresol



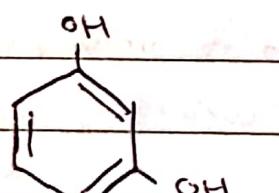
4-Methylphenol

p-cresol



Benzene-1,2-diol

catechol



Benzene-1,3-diol

Resorcinol

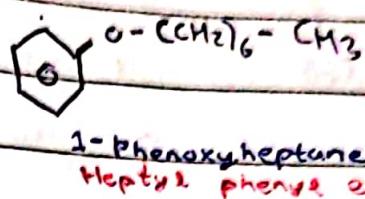
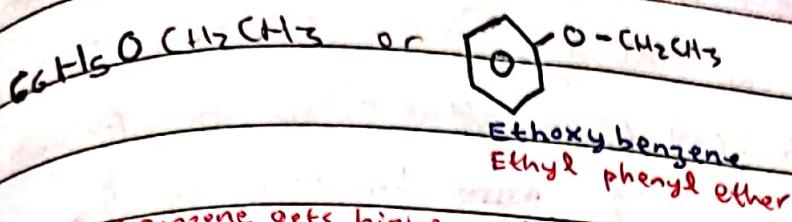


Benzene-1,4-diol

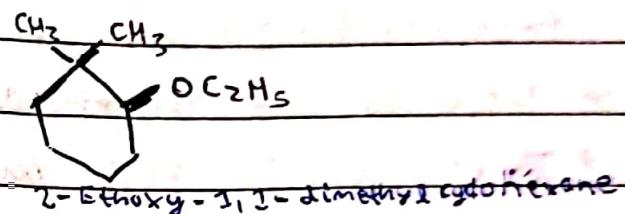
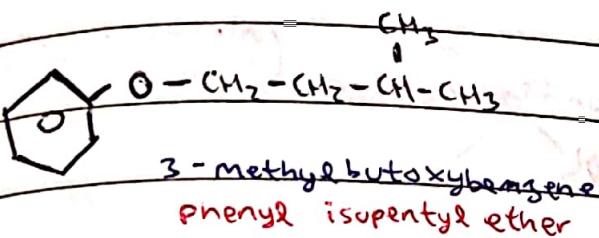
Hydroquinone or quinol

(iii) Ethers: $C_2H_5 - O - C_2H_5$
 Ethoxy ethane
 Diethyl ether

$CH_3 - O - CH_2 - CH_2 - CH_3$
 2-Methoxy propane
 Methyl propyl ether

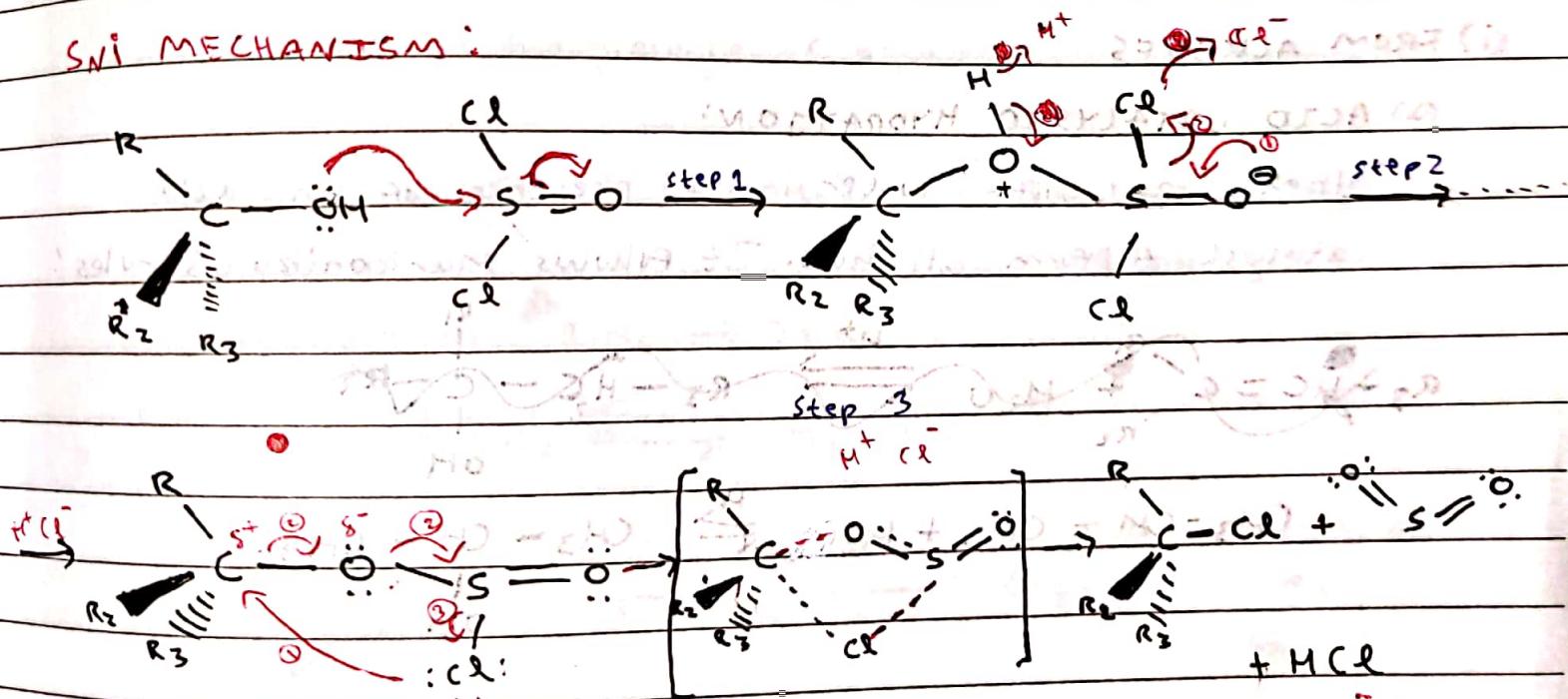


*note: Benzene gets higher priority over ethane since benzene has 6 carbons & ethane has 2, but in the second example Heptane (which has 7 carbons) gets higher priority over benzene. The general IUPAC rule is (Lesser priority group = oxy = Higher Priority Group)



JEE NOTES

SNI MECHANISM:



When pyridine is added to this mixture, S_N2 occurs. This is because pyridine (C_5H_5^-) attacks the sulphur at \bullet , displacing Cl^- and hence Cl^- performs back attack to displace sulphur's leaving group. This also leads to inversion of configuration

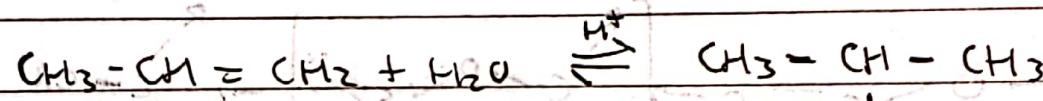
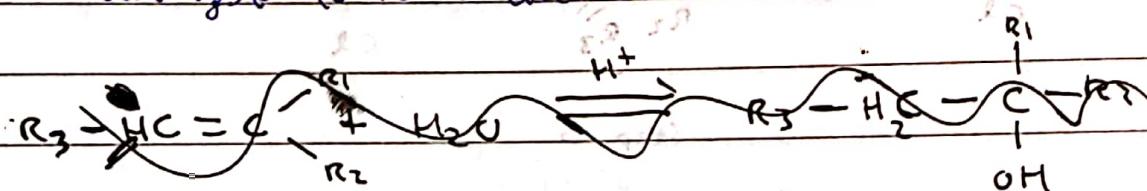
- S_Ni is a 3 step process.
- * It is favourable to carry out the reaction in a ~~protic~~ polar solvent.
- In protic polar solvent, the dissociated (cavide Cl⁻) will attract the polar solvent molecule.
- This hinders the dissociated Cl⁻ from attacking the polarized C intermolecularly. Instead the Cl⁻ bonded to S_N attacks the polarized C intramolecularly.
- * It is a 3 step process. There is no RNS, it is an extremely fast reaction.
- * There is 100% retention of configuration. (Makes it very useful)
- * It only takes place with SOCl₂

I: PREPARATION REACTIONS

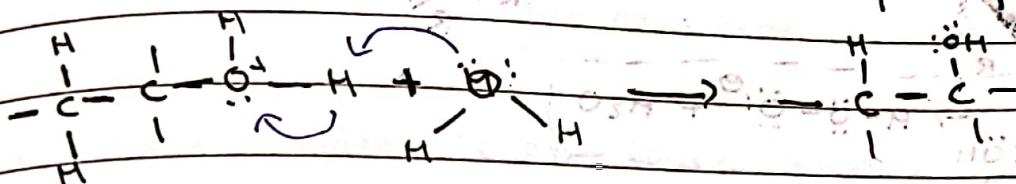
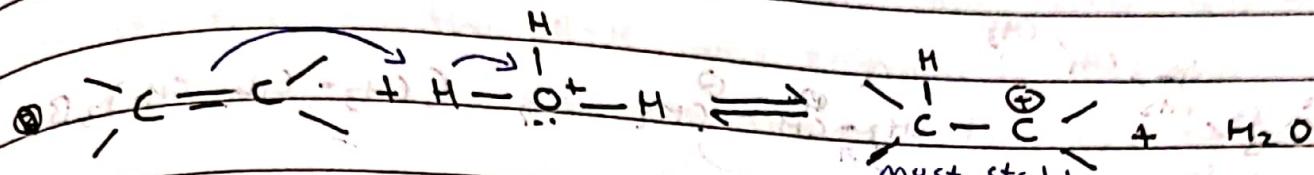
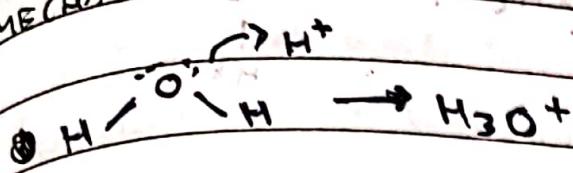
(i) FROM ALKENES

(a) ACID CATALYSED HYDRATION:

Alkenes react with water in the presence of an acid catalyst to form alcohols. It follows Markonikov's rules!

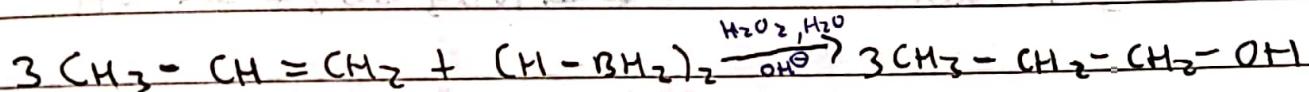


MECHANISM:



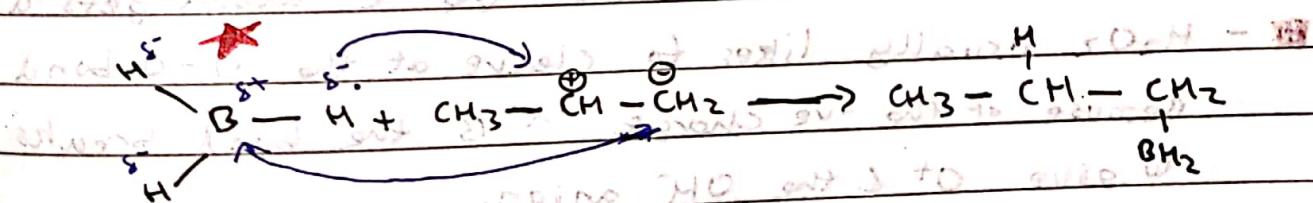
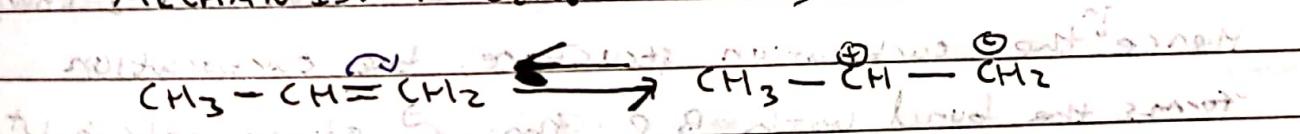
(b) HYDROBORATION-OXIDATION (Final product = Anti-markovnikov addition)

Diborane (BH_3)₂ reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.

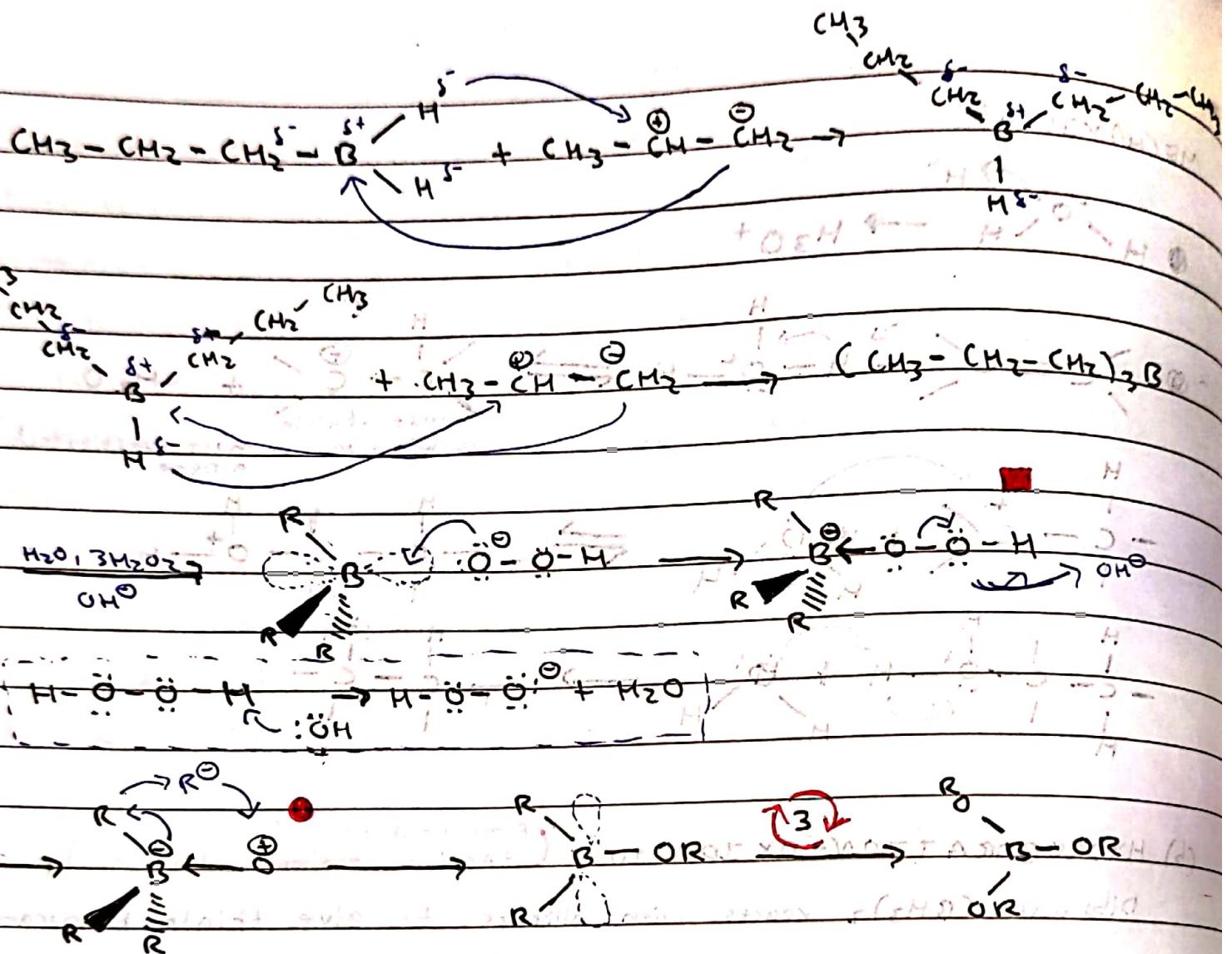


general: $\text{R}_1\text{R}_2\text{R}_3\text{CH}=\text{CH}_2 + \text{B}_2\text{H}_6 \rightarrow \text{R}_1\text{R}_2\text{R}_3\text{CH}_2-\text{CH}_2-\text{OH}$

MECHANISM: $\text{B}_2\text{H}_6 \rightarrow 2\text{BH}_3$ o 2nd & 3rd



general: $\text{R}_1\text{R}_2\text{R}_3\text{CH}=\text{CH}_2 + \text{B}_2\text{H}_6 \rightarrow \text{R}_1\text{R}_2\text{R}_3\text{CH}_2-\text{CH}_2-\text{OH}$

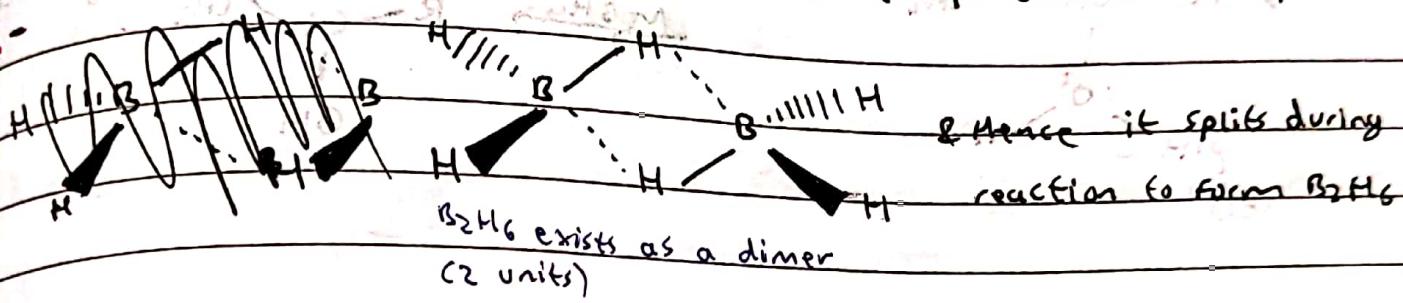


★ - B is more electronegative than hydrogen and hence in BH_3 B has a net $\delta+$ charge & H has the $\delta-$ charge. Hence in the carbocation structure, the carbocation forms the bond with B & the δ atom gets attached.

★ - H_2O_2 usually likes to cleave at the O-O bond. Because of the -ve charge on B the bond breaks to give O^\cdot & the OH^- anion.

★ - Alkyl shift takes place. O has +ve charge & is hence

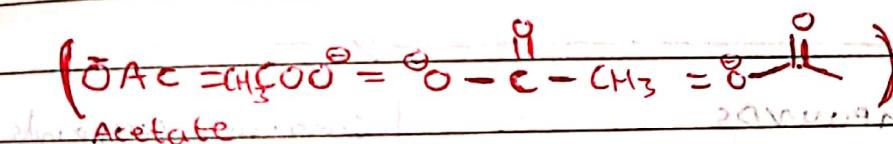
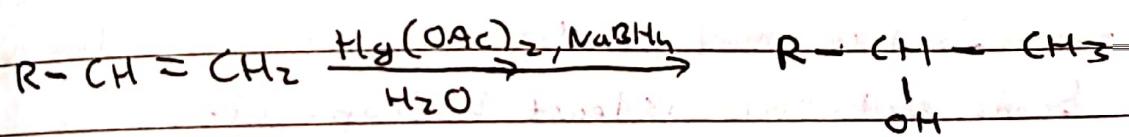
an electron deficient species. Hence it attracts the electrons in the β -R bond. This causes the entire $\bullet R^{\ominus}$ - alkyl group to shift over & bond with O^{\oplus} cation. Also, since B is much bigger than O, the B-R bond enthalpy is less than O-R bond enthalpy. Thus this rearrangement process takes place.



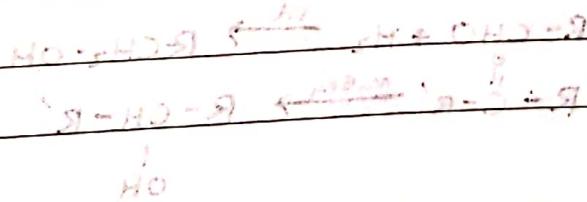
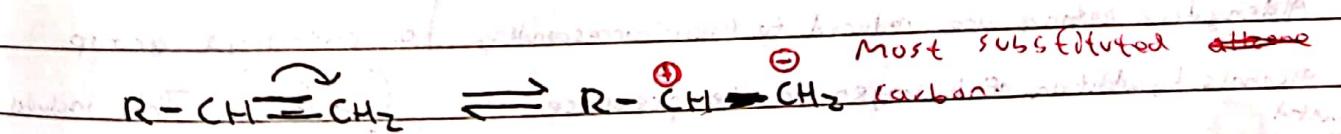
*Note: The end product is essentially what appears to be the product of anti-Markovnikov's addition of H_2O .

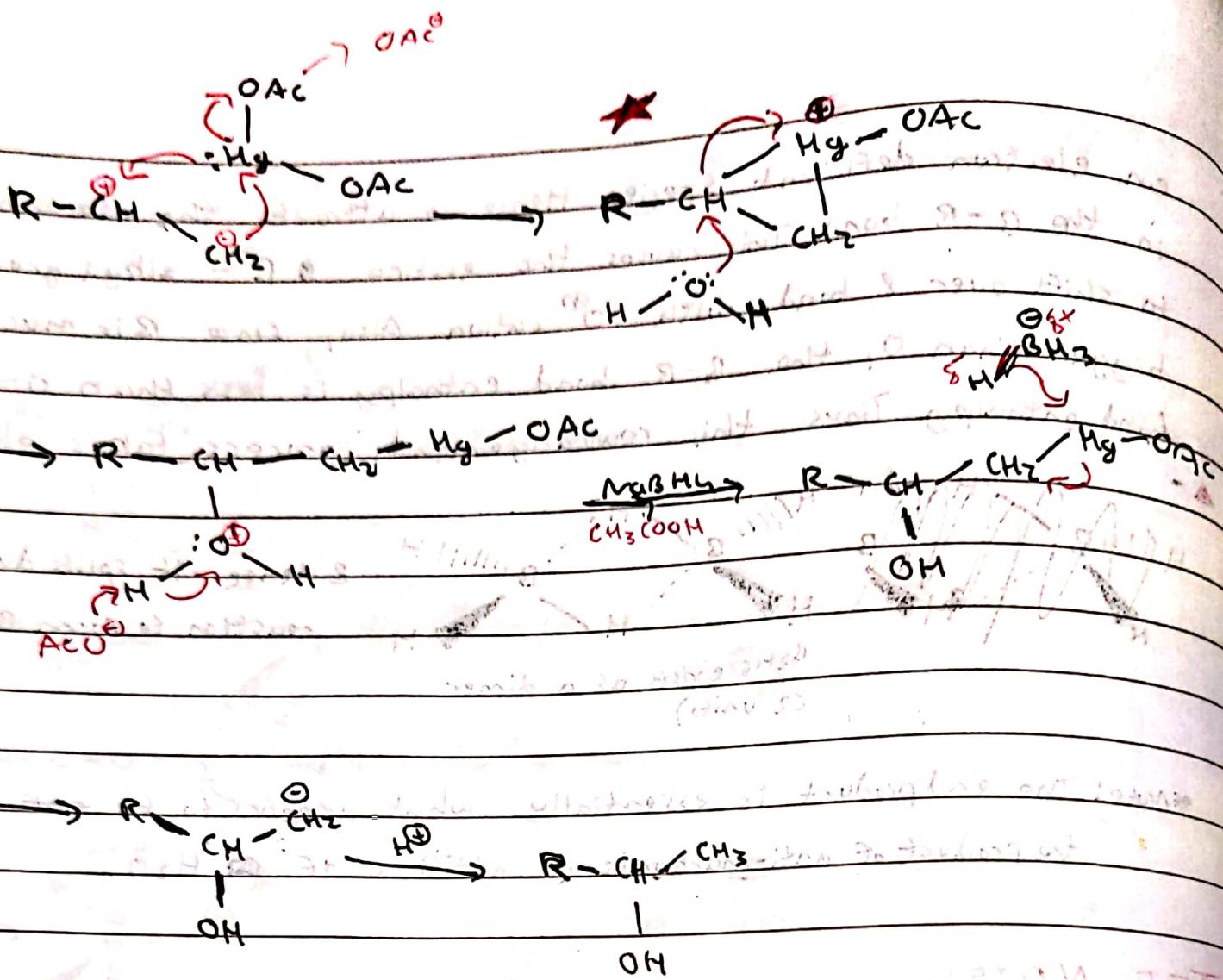
JEE NOTES

OXYMERCURATION-DEMERCURATION (\rightarrow Markovnikov's Addition)



MECHANISM:



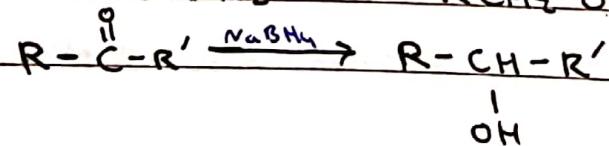
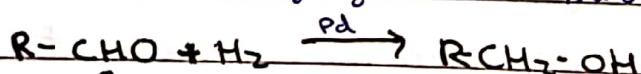


*- Water attacks most substituted carbon because (-H bond) is hydrophobic, and the most substituted carbon has least C-H bonds and hence is least hydrophobic.

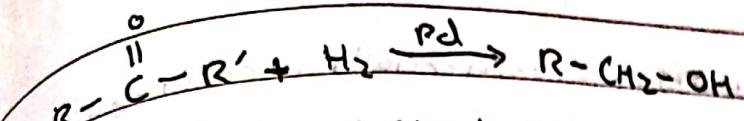
(ii) FROM CARBONYL COMPOUNDS

(a) REDUCTION OF ALDEHYDES & KETONES

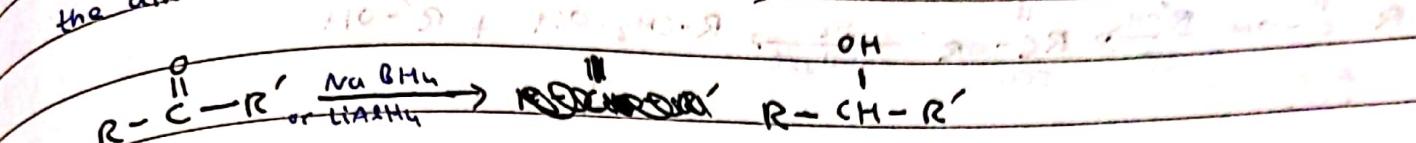
Aldehydes & ketones are reduced to their corresponding alcohols by addition of hydrogen in the presence of metal catalysts such as Pt, Pd, Ni or by treating them with strong reducing agents like NaBH₄ or LiAlH₄.



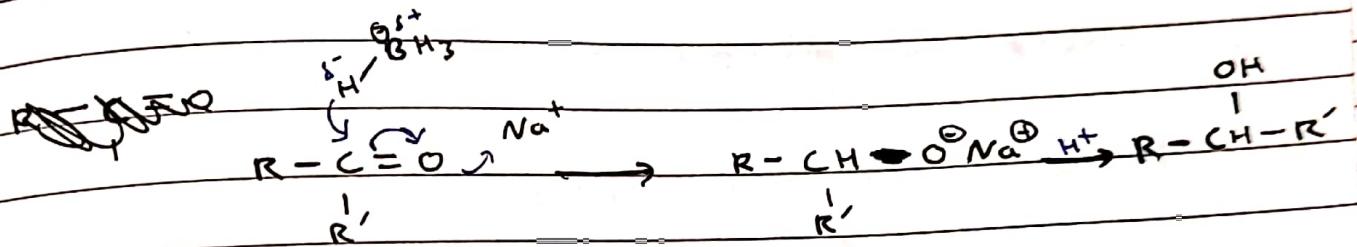
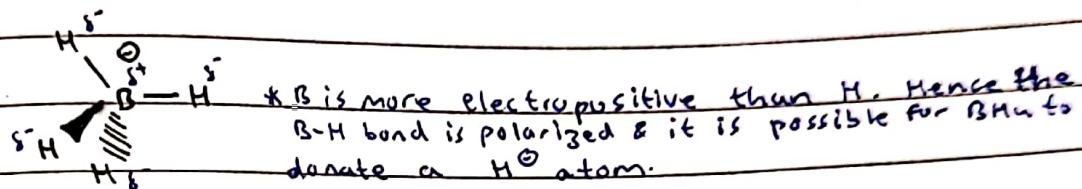
Carbonyl compounds are compounds containing a carbonyl group (C=O). This includes aldehydes, ketones, carboxylic acids & esters.



reaction follows standard addition of H_2 mechanism. [Metal cleaves H-H bond & $\text{C}=\text{O}$ double bond. Then the H atoms are transferred to the alkene & final product is formed]



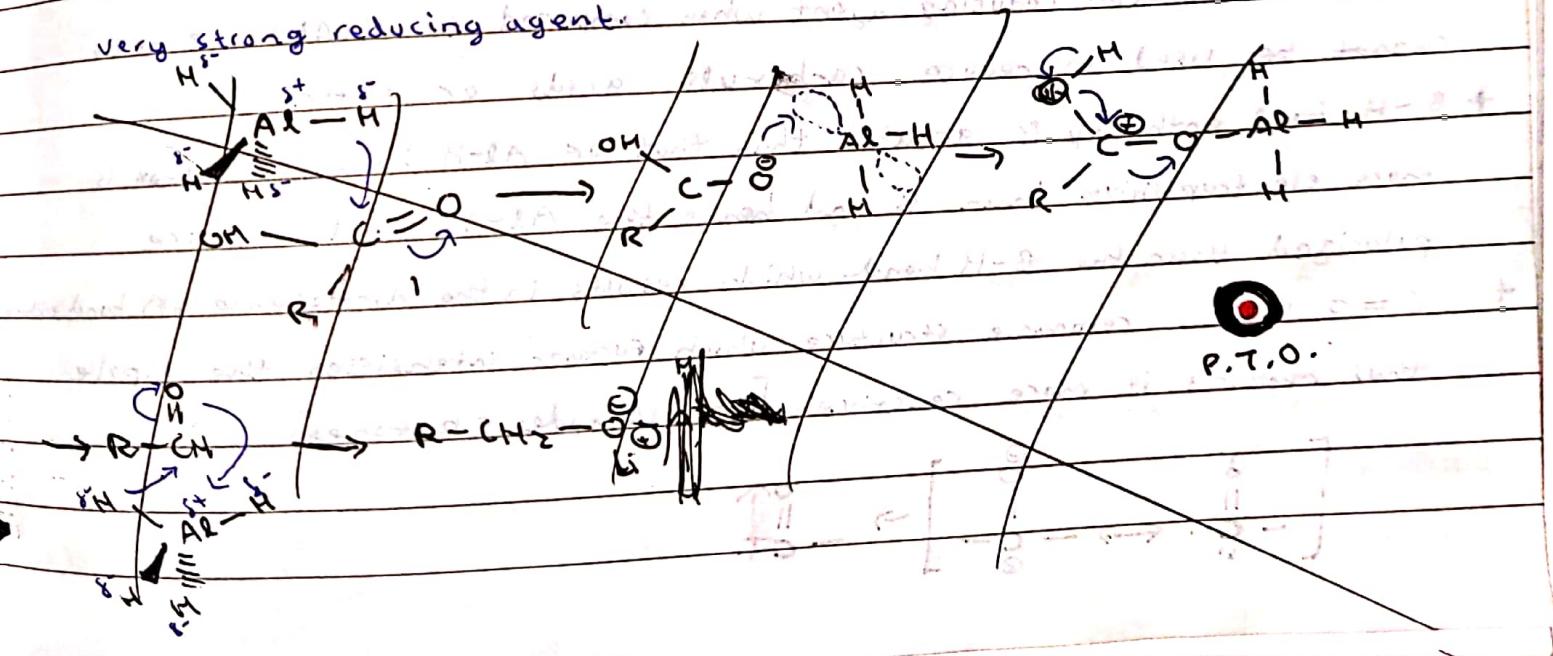
MECHANISM:



(b) REDUCTION OF CARBOXYLIC ACIDS & ESTERS

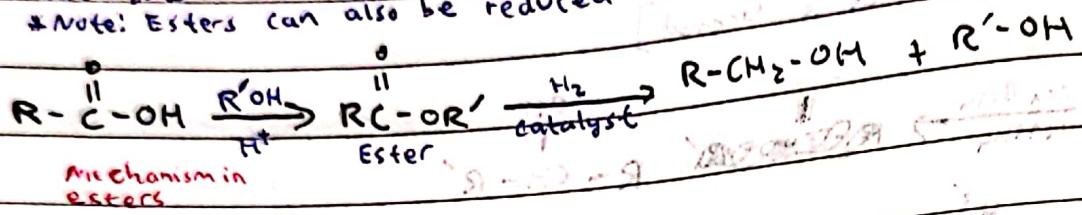
① Carboxylic acids are reduced to primary alcohols ($\text{R}-\overset{\text{O}}{\text{C}}-\text{OH} \rightarrow \text{R}-\text{CH}_2-\text{OH}$)

in excellent yields by lithium aluminium hydride (LiAlH_4) which is a very strong reducing agent.



- ② However, LiAlH₄ is expensive and therefore, commercially, carboxylic acids are usually first converted to esters & then reduced using hydrogen catalysts.
- * Note: Esters can also be reduced to Alcohols via reduction with NaBH₄.

Acids are usually first converted to catalysts.
*Note! Esters can also be reduced to Alcohols via reduction with BH_3THF .

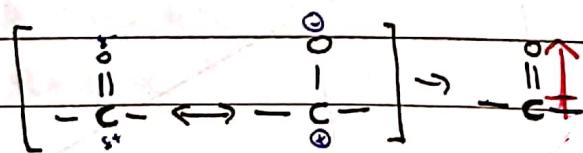


Mechanism in esters

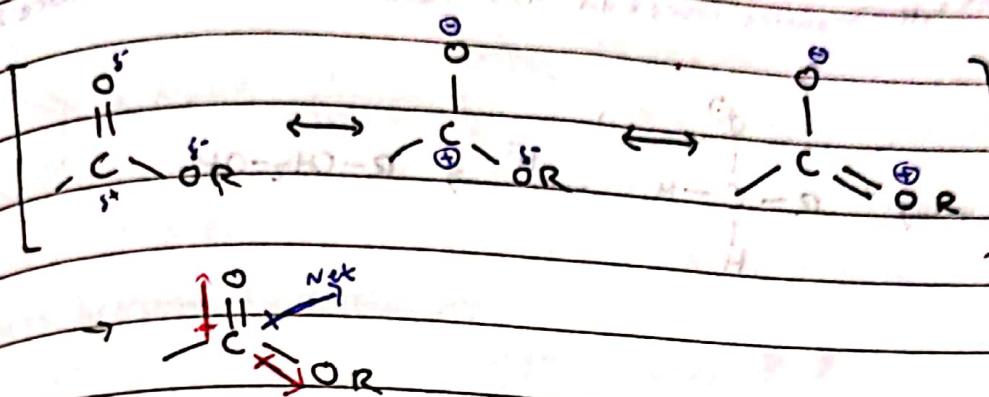
2000-10-27 10:00 AM - 10:30 AM H-9
H-9 H-9 H-9 H-9 H-9 H-9 H-9 H-9 H-9

Liam vs Nabith

- + NaBH_4 is a weaker reducing agent when compared to LiAlH_4 & hence cannot be used to reduce carboxylic acids or esters.
- + B-H bond enthalpy is greater than that of Al-H because Al^{+3} is more electropositive than B and hence the Al-H bond is more polarized than the B-H bond which results in the difference in bond length.
- + C=O has a resonance structure which further intensifies the dipole thus making it more reactive. [In aldehydes & ketones]

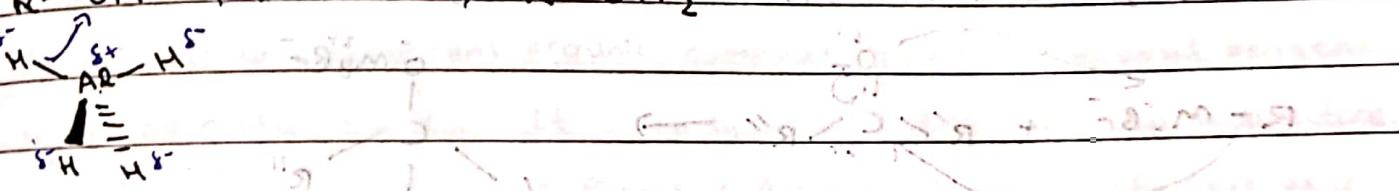
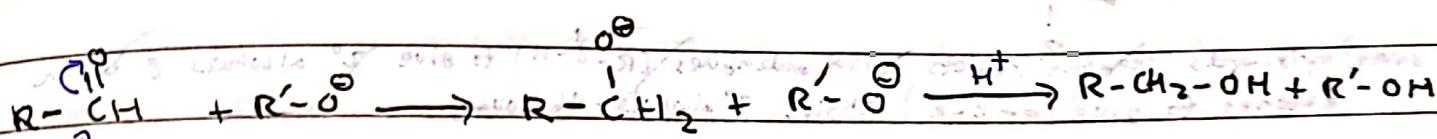
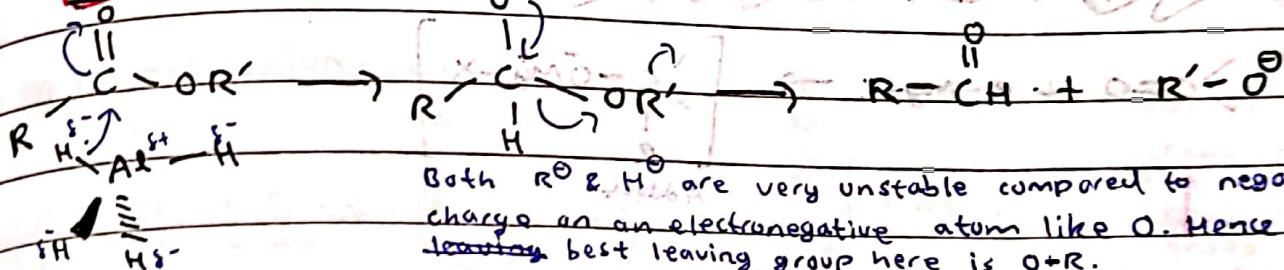


+ In esters and carboxylic acid's the resonance structures reduce its reactivity by negating the dipole moment.

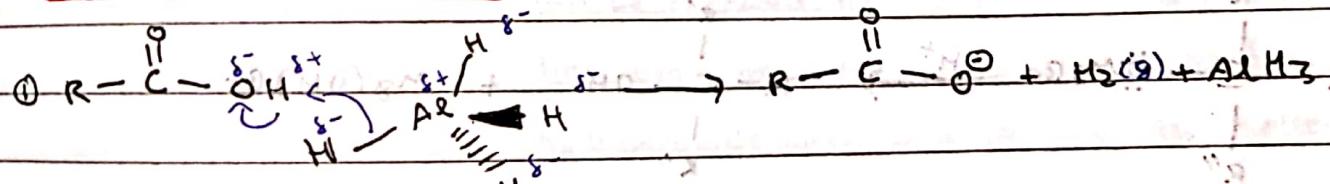


REDUCTION OF CARBOXYLIC ACIDS & ESTERS BY LiAlH₄

ESTERS

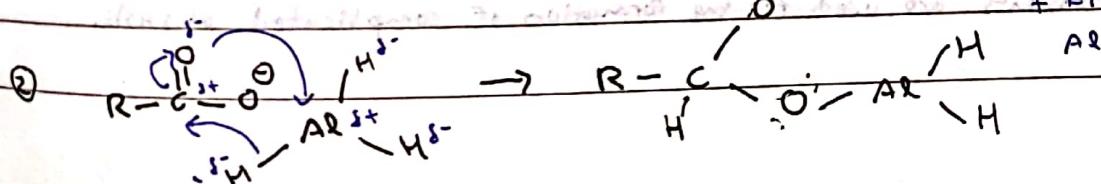


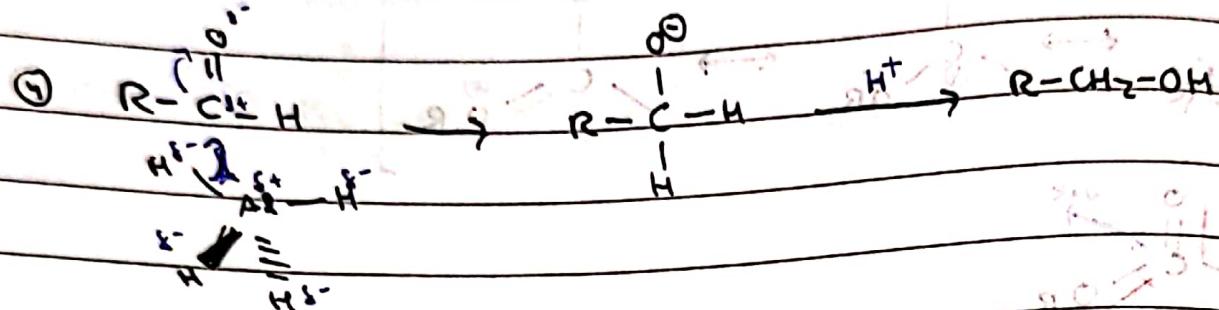
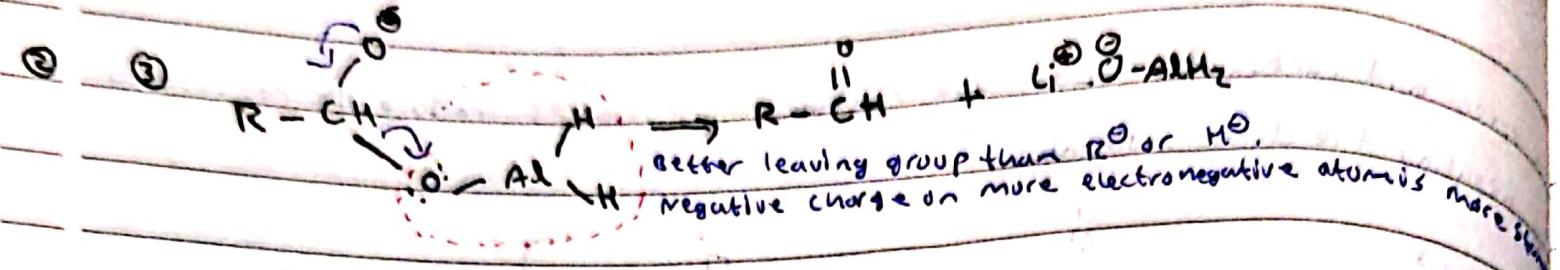
CARBOXYLIC ACIDS



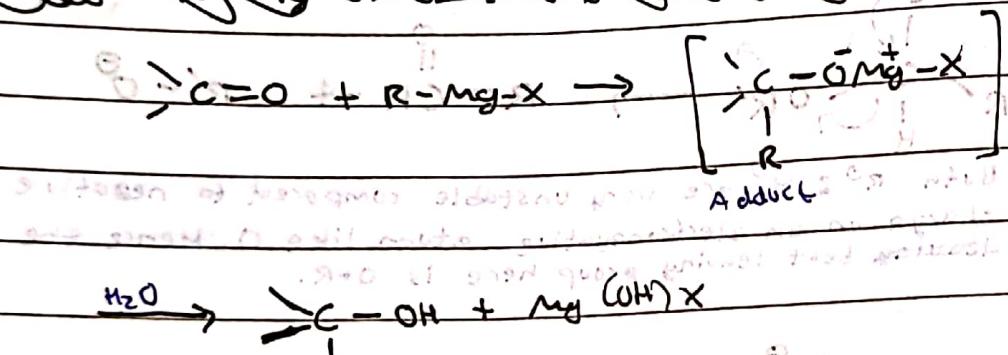
or H_2O deprotonates it & forms H_3O^+ . H_3O^+ is also a product here.

either O^0 or H^0 can attack

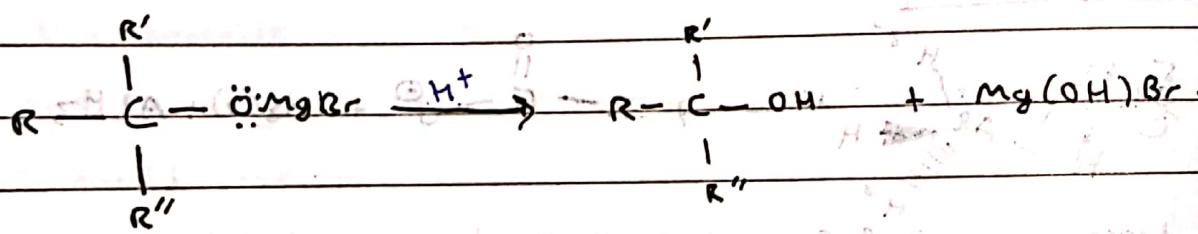
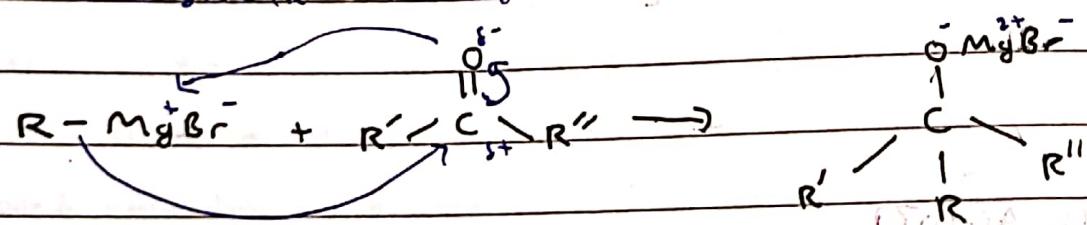




(iii) From GRIGNARD REAGENTS



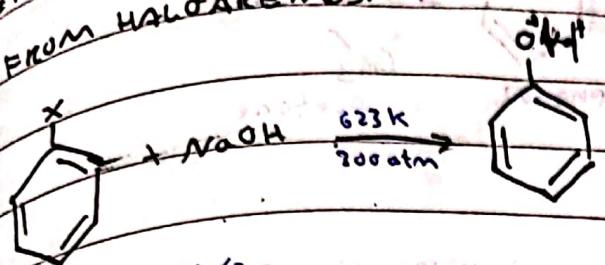
*Note: Grignard reagent reacts with aldehydes ($\text{R}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}} \text{H}$) to give 2° alcohols & with ketones to give ($\text{R}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{R}'$) to give 3° alcohols. Obviously.



*Note: Grignard reagents are used for the formation of complicated alcohols.

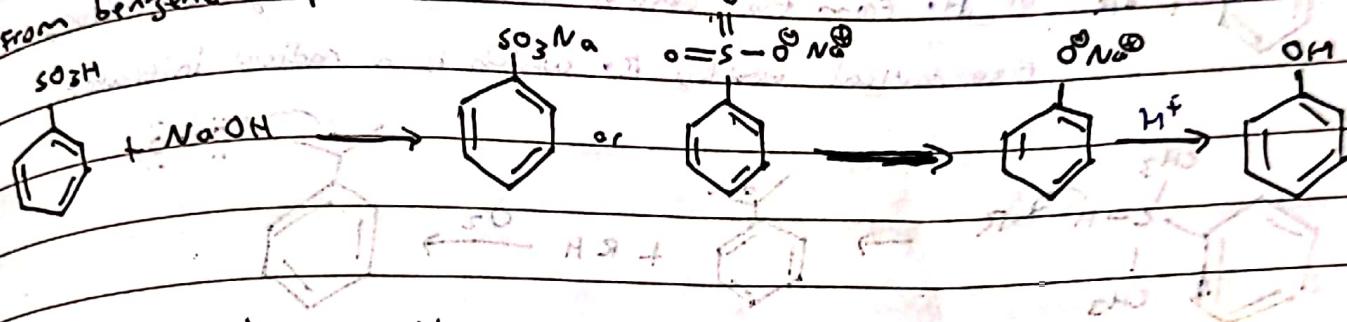
PREPARATION OF HALOARENES

(a) FROM HALOARENES.

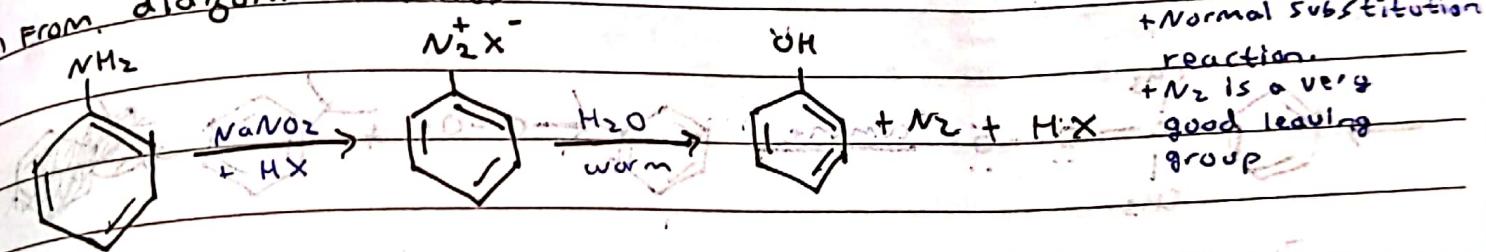


Elimination-addition mechanism
or by addition-elimination reaction at lower
temp & pressures for activated substituted
benzene rings, aryl halides.

(b) from benzene sulphonic acid



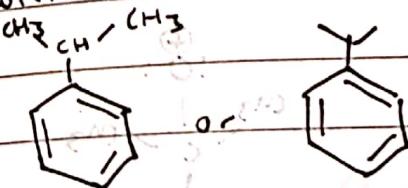
(c) From diazonium salts



(d) From cumene

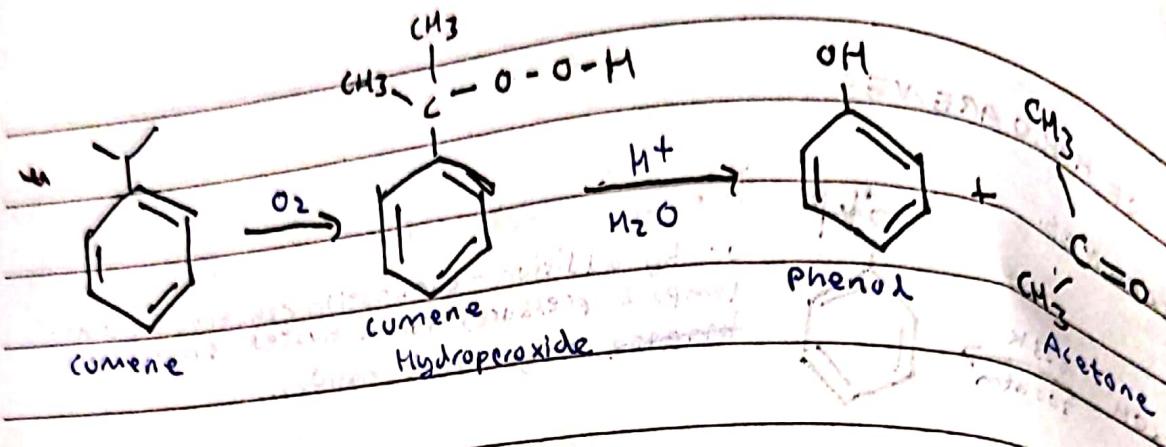
Cumene is an important organic compound called isopropyl benzene

with formula C_9H_{12} . It is mainly used for the industrial manufacture



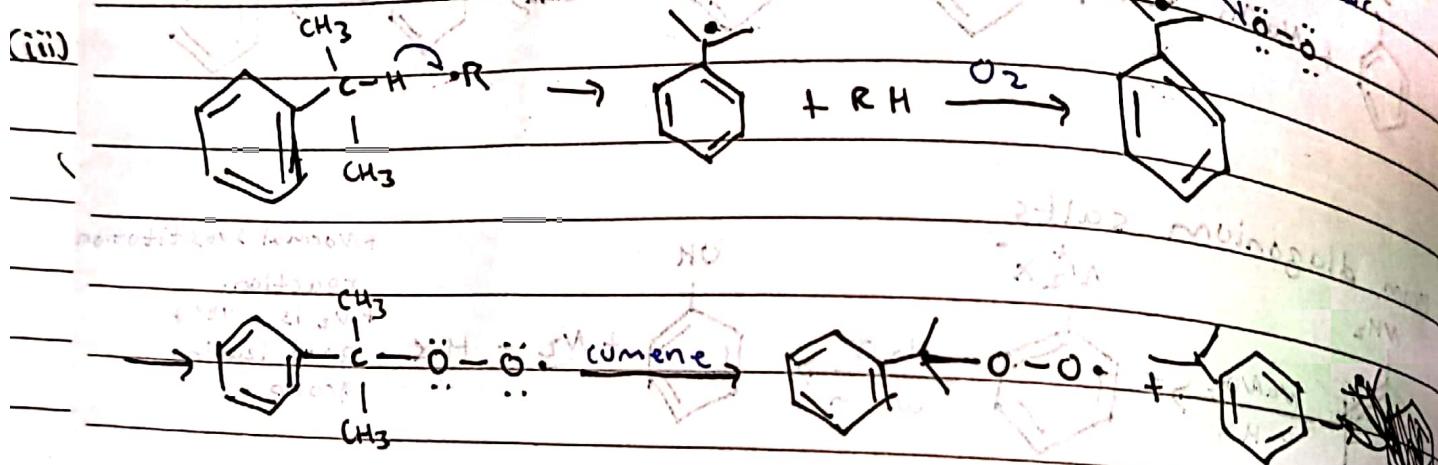
of Phenol & Acetone. It is cost-effective as it
can be prepared from cheap starting materials

like benzene. Cumene can be air oxidized to cumene
hydroperoxide which is further acidified to phenol &
acetone.

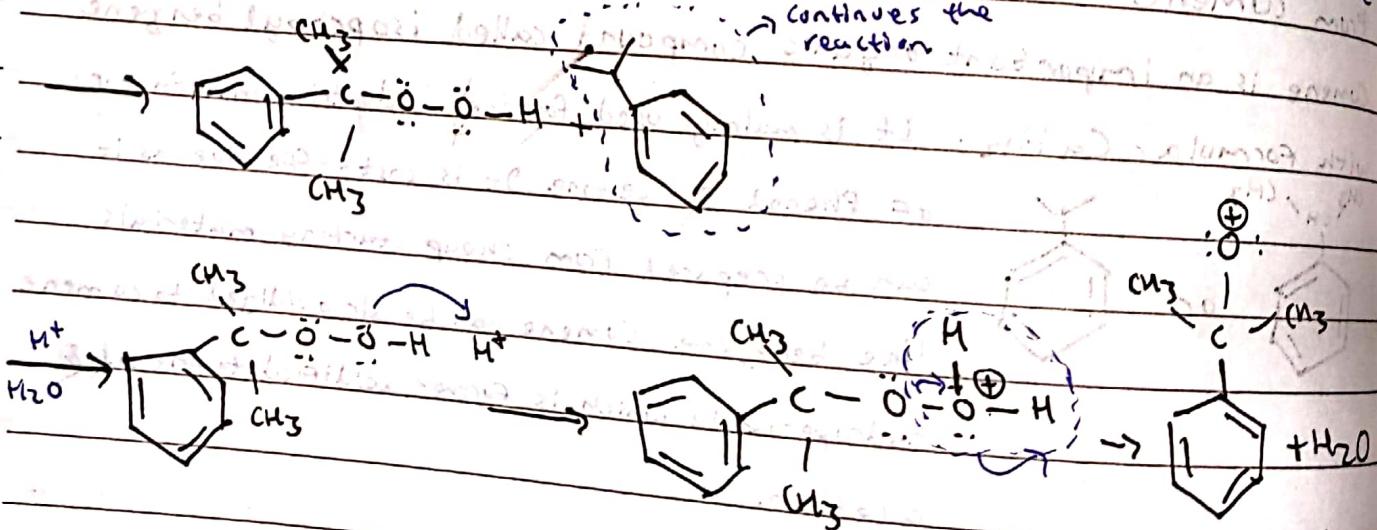


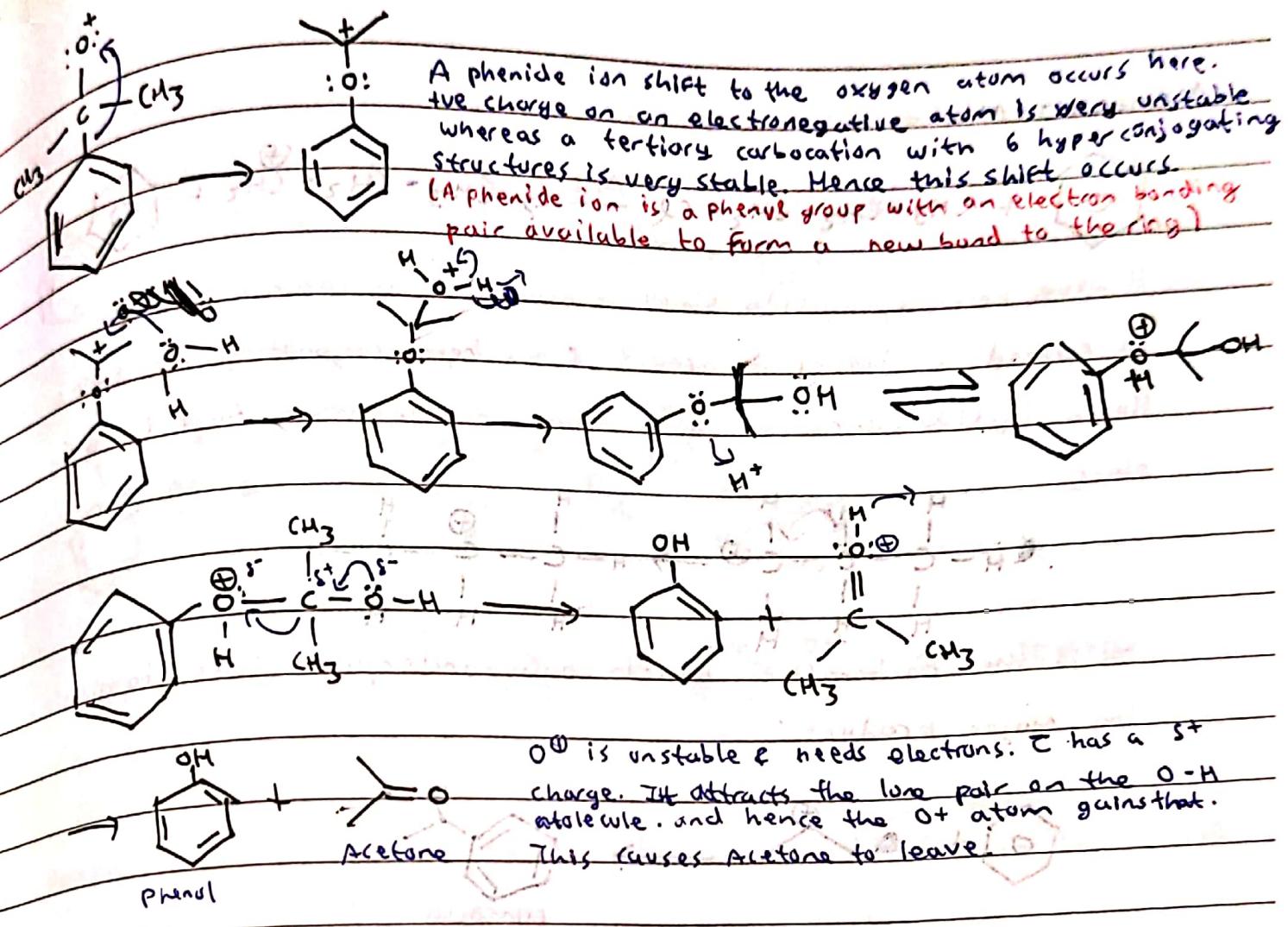
MECHANISM

The first step of this process involves the abstraction of H^+ from the central C atom creating a tertiary free radical which is a radical initiator.



The free radical on an electronegative atom like O makes it a powerful radical initiator & hence it abstracts a H^+ from another cumene molecule thus creating a chain reaction.

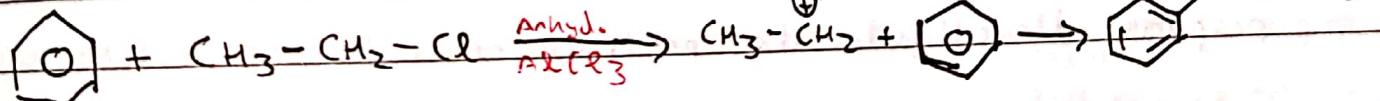




JEE NOTES

Friedel-Crafts alkylation & acylation work on benzene. This can be used to synthesize cumene ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$). When performing the alkylation with longer hydrocarbon chains we must take into account the possibility of rearrangement of carbocation for stability. This is possible only if we follow along with the mechanism.

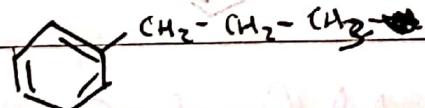
EAS reaction



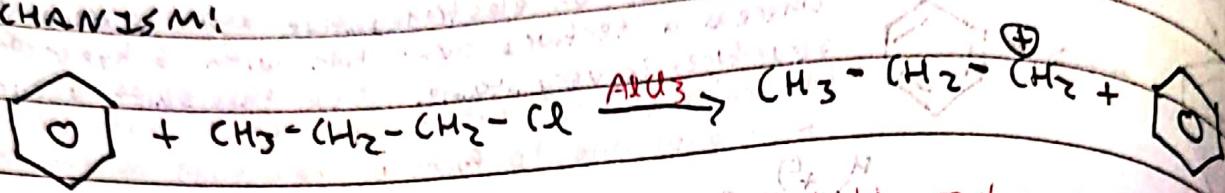
However, with longer chain hydrocarbons like ~~or propene~~ chloropropane

($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$) the major product is not

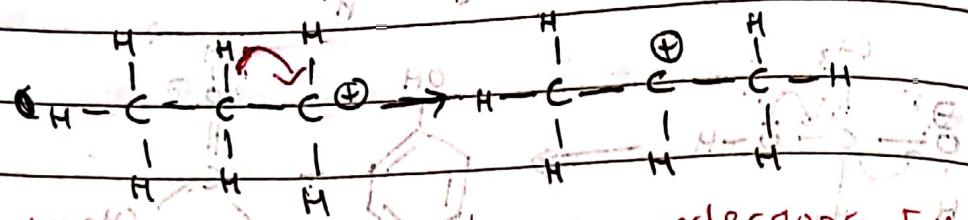
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$



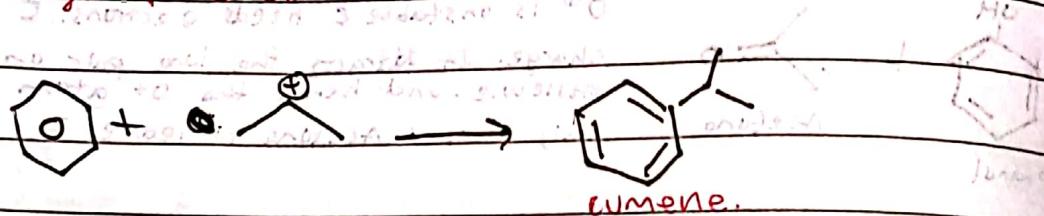
MECHANISM:



However here, by hydride shift a more stable carbocation can be formed. +1 inductive effect & +4 hyperconjugating structure. Hence hydride shift, i.e., carbocation rearrangement first takes place.



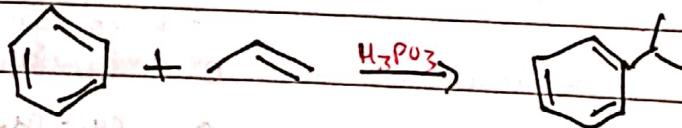
It is this carbocation which now undergoes EAS to give the major product:



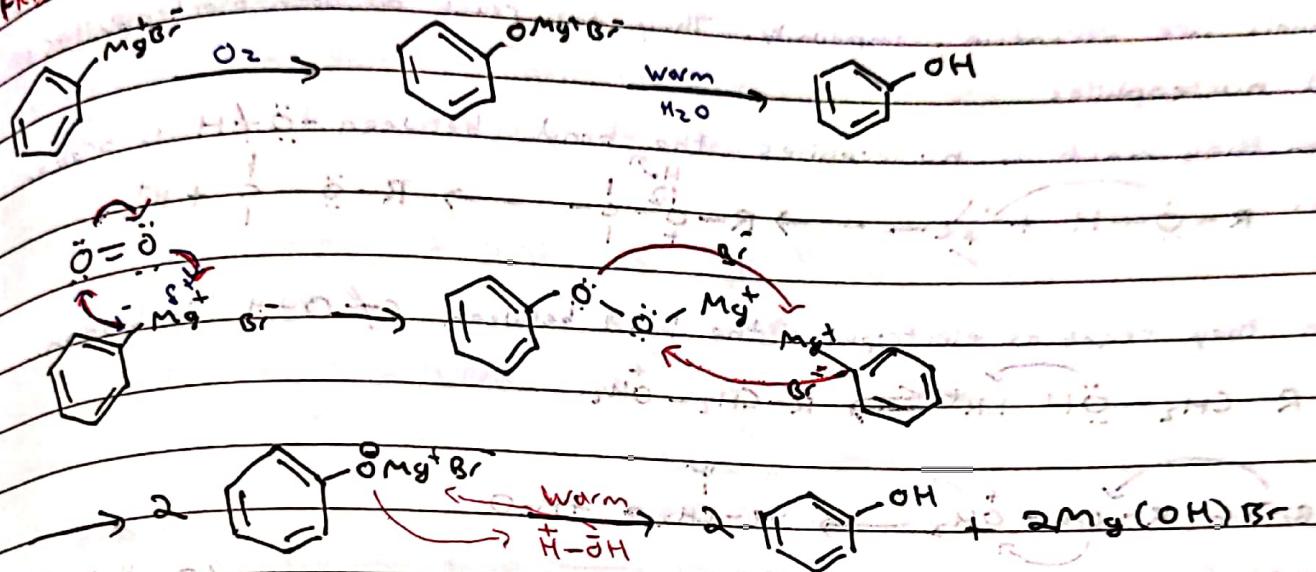
PREPARATION OF CUMENE

* Cumene can be formed by the alkylation of ~~prop~~ 1-chloro-propene as shown above or by reacting propene ($\text{CH}_3-\text{CH}=\text{CH}_2$) with a mineral acid like HCl to give α -chloropropene ($\text{CH}_3-\overset{\text{Cl}}{\underset{\text{C}}{\text{C}}}-\text{CH}_3$) by Markovnikov's rule & then performing alkylation.

* We can also form cumene by reacting benzene with propene directly in the presence of catalyst H_3PO_3

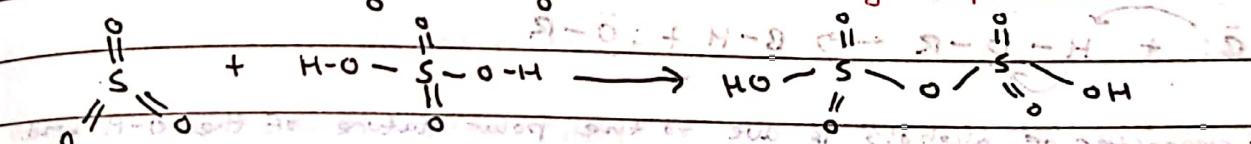


PREPARATION OF PHENOL FROM GRIGNARD'S REAGENTS IN CONCERT



PREPARATION OF BENZENE-SULPHONIC ACID ($C_6H_5SO_3H$) WITH OLEUM

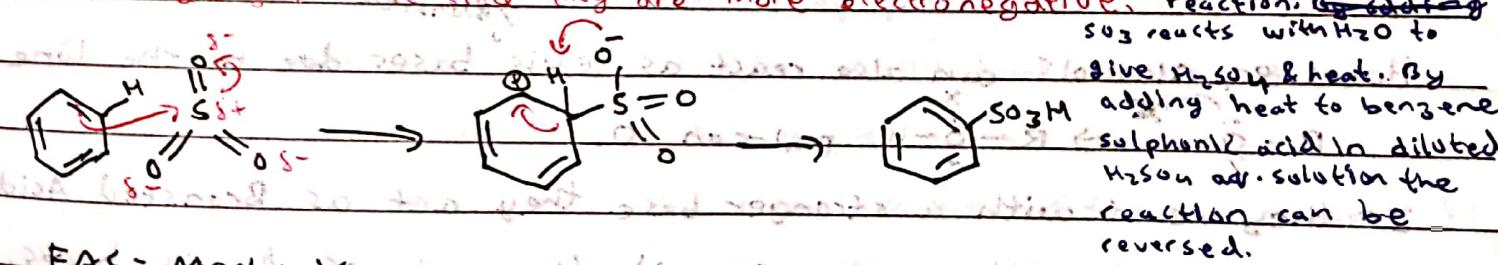
OLEUM ($HO-S(=O)(=O)-O-H$) or fuming sulphuric acid



SO_3 + H_2SO_4 Sulphur trioxide + Sulphuric acid \rightarrow Oleum (pyrosulphuric acid)

Oleum is a concentrated solution of dissolved sulfur trioxide in sulfuric acid. The sulfur in SO_3 is electrophilic because the oxygens pull electrons away from it since they are more electronegative.

This is a reversible reaction. By adding SO_3 reacts with H_2O to

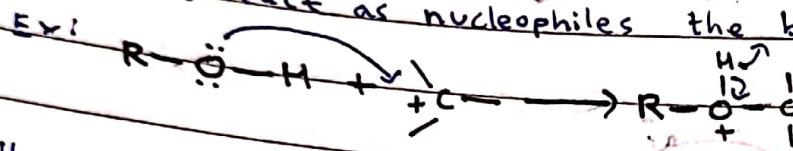


EAS - Mechanism for weak acids \times to strong acids \times

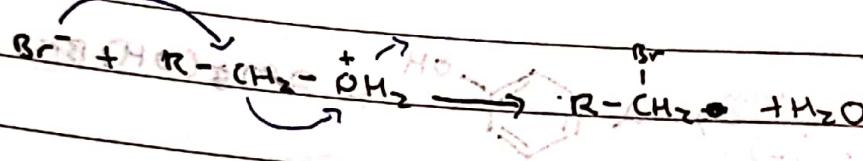
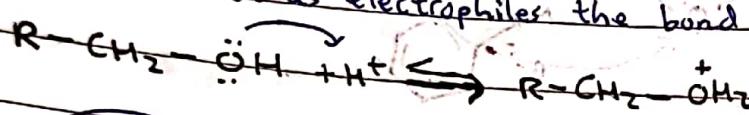
REACTIONS WITH R-OH

Alcohols are versatile compounds. They can react as both electrophiles and nucleophiles.

+ When they react as nucleophiles the bond between $\ddot{\text{O}} + \text{H}$ is broken.

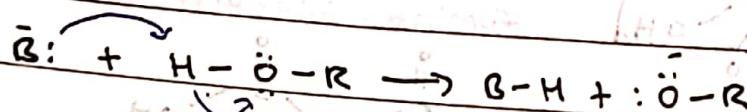


+ When they react as electrophiles the bond between $\text{C} + \text{O}-\text{H}$ is broken.

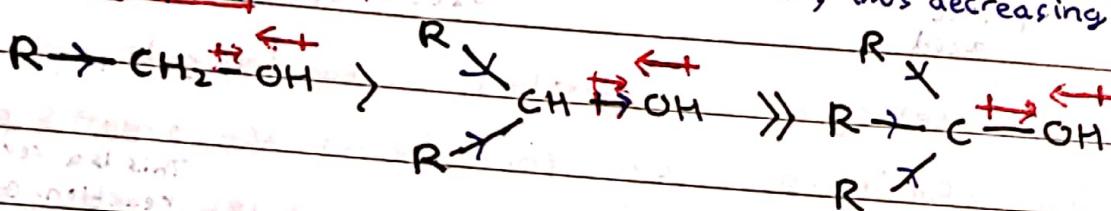


REACTIONS INVOLVING R-OH ACTING AS NUCLEOPHILE

Alcohols & Phenols are slightly acidic in nature. They are Bronsted acids, i.e., they can donate a proton to a stronger base (B^-)



The acidic character of alcohol's is due to the polar nature of the $\text{O}-\text{H}$ bond. Electron releasing groups ($-(\text{CH}_3, -\text{C}_2\text{H}_5)$ etc) increase electron density on oxygen & hence tend to lower the polarity of $\text{O}-\text{H}$ bond, thus decreasing acid strength. (decrease dipole)

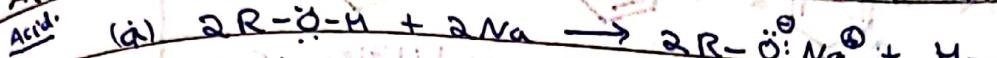
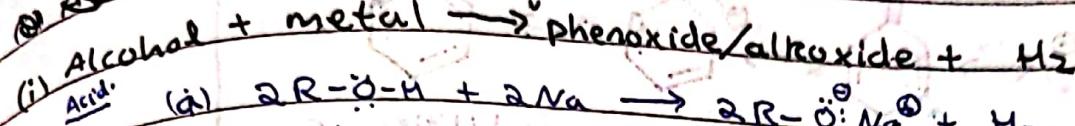


However, Alcohols can also react as Lewis' bases due to the lone pair on O.

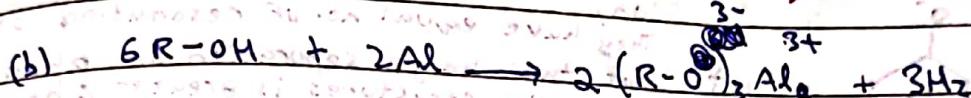
If they react with a stronger base they act as Bronsted Acids.
If they react with a stronger acid they act as Lewis bases.

ACIDIC REACTIONS

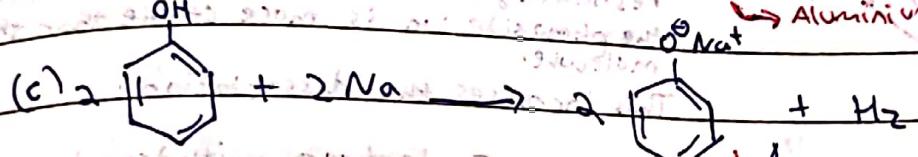
(i) ~~Alcohol + metal~~ → metal



→ Sodium alkoxide

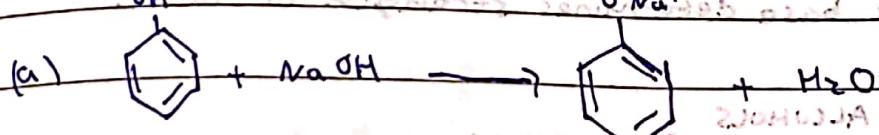


→ Aluminium alkoxide



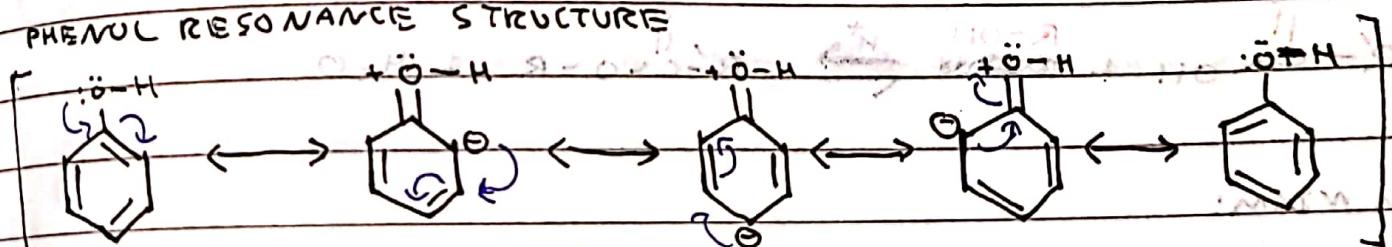
→ Sodium phenoxide

(ii) ~~Alcohol + stronger base~~ → ~~Alkoxide/phenoxide salt + Base-H~~



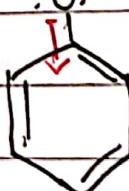
*Note: Alcohols are weaker acids than water, i.e., they are stronger bases than water & hence act as

PHENOL RESONANCE STRUCTURE



Phenols are stronger acids than alcohols.

:O: ↓ Benzene acts as an electron withdrawing group thus decreasing charge density on O & increasing polarity of OH bond. (Increases dipole)



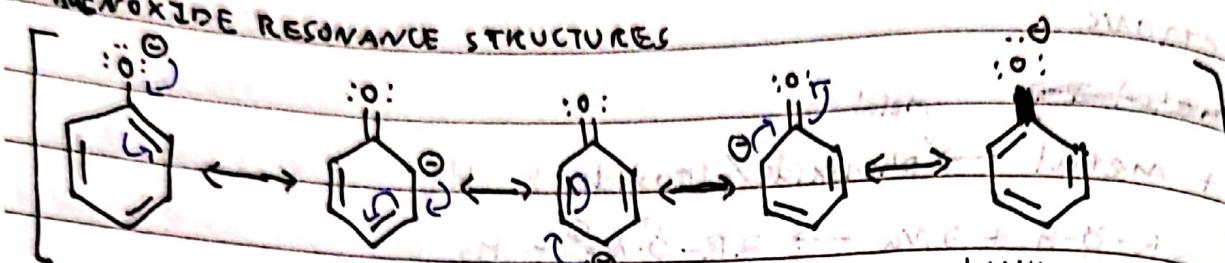
Hence there is higher ionisation of phenols than alcohols.

The resonating structures causes the oxygen of the -OH group to be

positive. Hence it is

Hence phenols cannot act as Brønsted or Lewis Bases

PHENOXIDE RESONANCE STRUCTURES



Comparing the stabilities of phenol & phenoxide ion, they have equal no. of resonating structures but the charge separation in phenols is greater & hence the phenoxide ion is more stable than the phenol molecule.

This increases the dissociation.

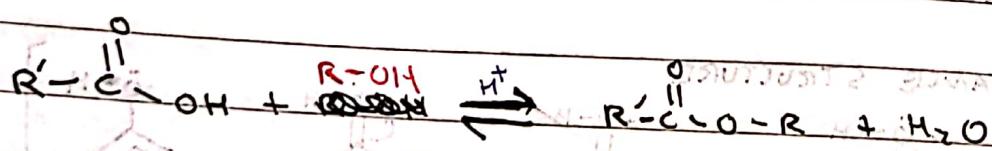
In substituted phenols, the presence of electron withdrawing groups like NO_2 at ortho & para positions increases acidity whereas electron donating groups like CH_3 would reduce acidity.

* Stability of conjugate base determines strength of acid.

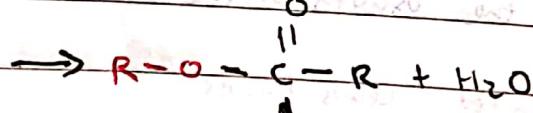
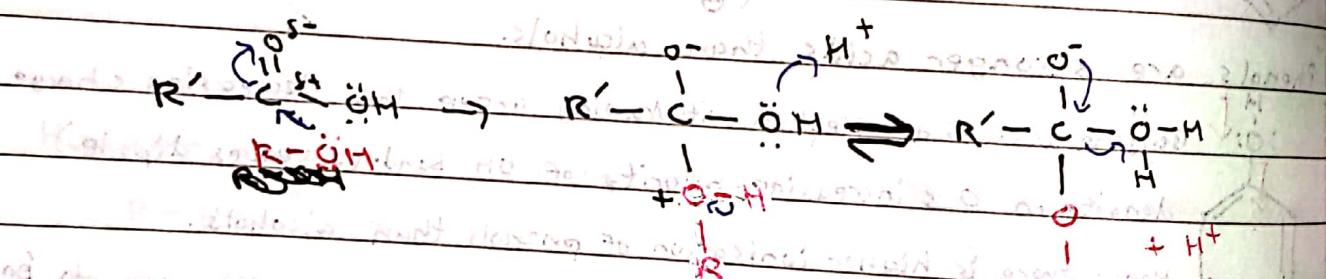
ESTERIFICATION OF ALCOHOLS & PHENOLS

$\text{R}-\text{OH}$ can either be an alcohol or a straight phenol.

(i) WITH CARBOXYLIC ACIDS

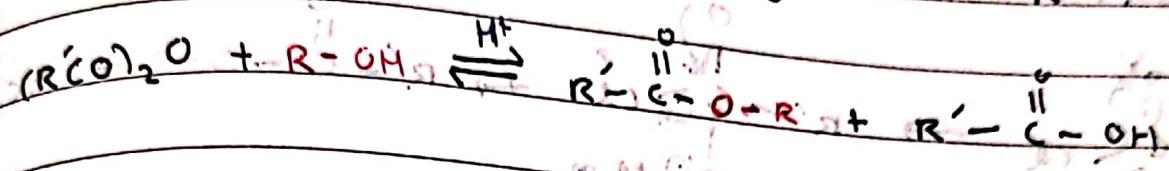
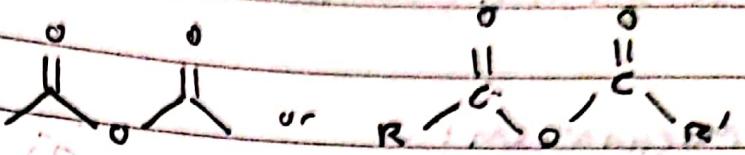


Mechanism:

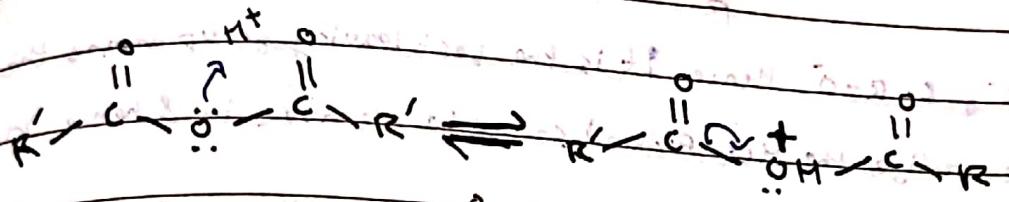


(ii) WITH ACID ANHYDRIDES

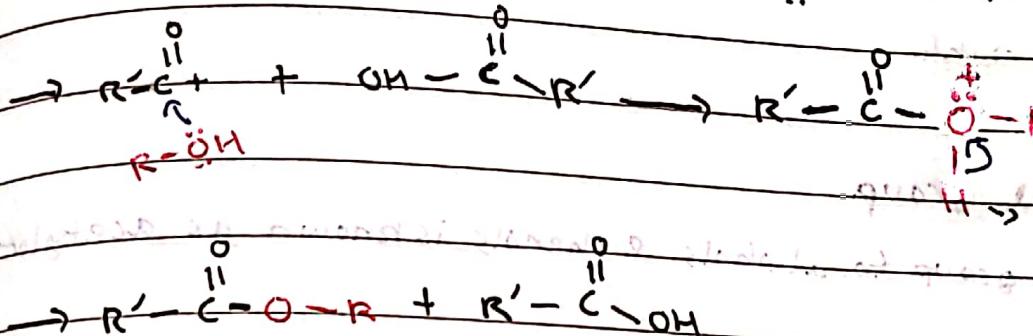
Acid anhydride \rightarrow $(RCO)_2O \downarrow$



MECHANISM:

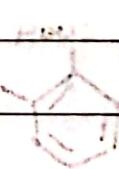
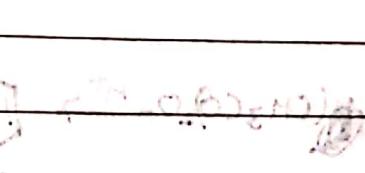
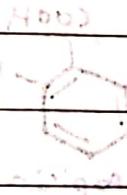


+ Generally, we use symmetric acid anhydrides & hence the product formed is the same no matter which carbocation is formed. If you use asymmetric acid anhydride major product will be that compound which forms the more stable carbocation.

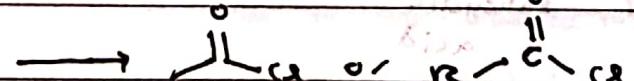


+ The reactions with carboxylic acid and acid anhydrides involves protonation of O & hence these ~~steps~~^{reactions} are reversible. So, water is usually removed as soon as it is formed to drive the equilibrium in the forward direction.

(iii) WITH ACID CHLORIDES

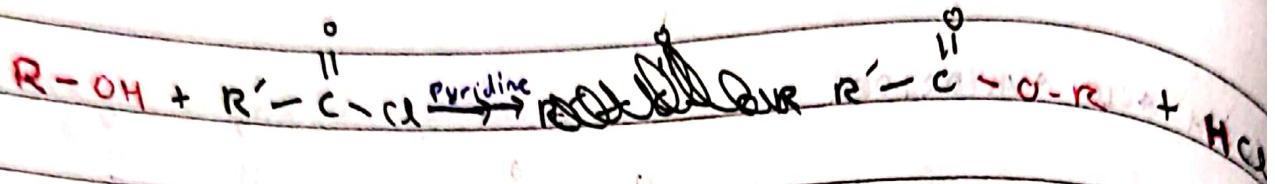


Acid chloride \rightarrow ~~O-~~ RCOCl

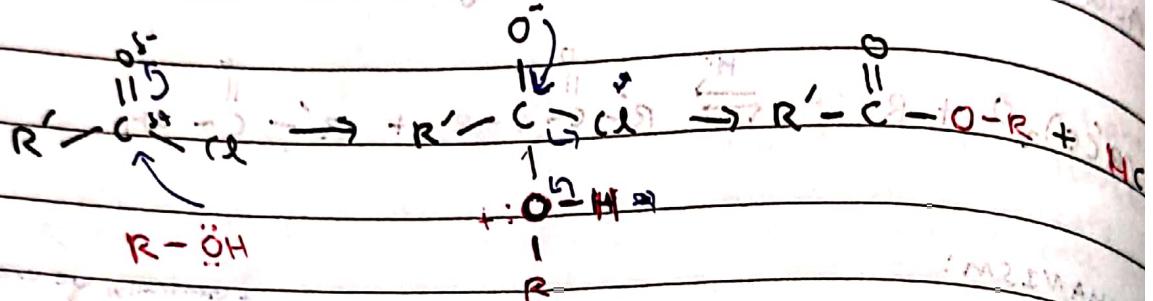


Pyridine → ~~Pyridine~~





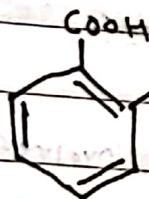
MECHANISM:



$+Cl^-$ is more stable than R^- & $R-O^-$. Hence it is the best leaving group among the three. Pyridine is added to neutralize the HCl formed so as to remove it & hence drive the equilibrium to the right.

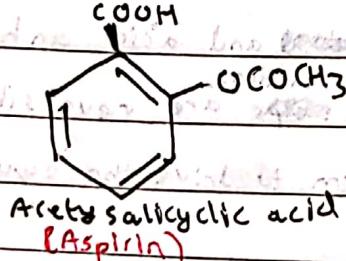
$CH_3CO \rightarrow$ Acetyl group.

Addition of acetyl group to alcohols & phenols is known as acetylation.

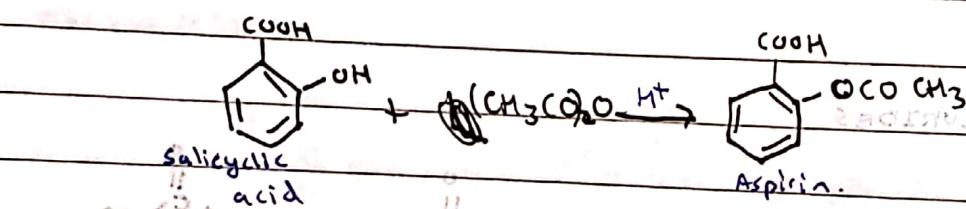


Acetylation of salicylic acid produces aspirin.

Salicylic acid
only when OH is
at ortho position is
it called Salicylic
acid.



Acetylsalicylic acid
(Aspirin)

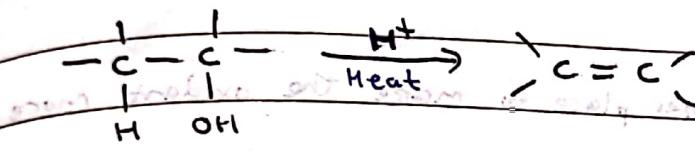


(ii) REACTIONS INVOLVING CLEAVAGE OF $(C-OH)$ bond
(Acting as Electrophiles)

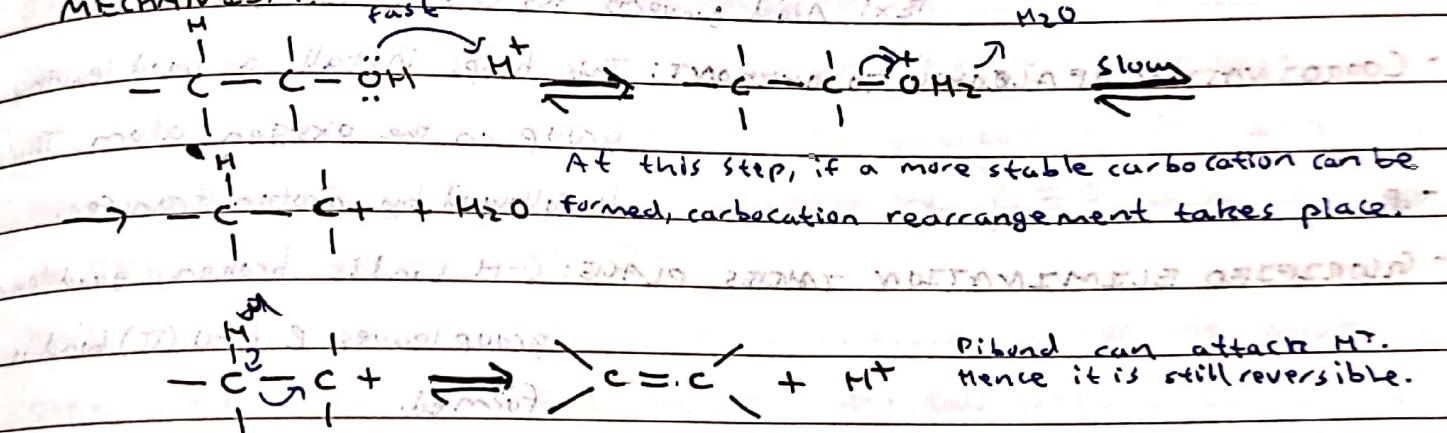
(a) Reactions of alcohols to form alkyl halides.
(covered in chap 2)



(b) Dehydration



MECHANISM: relatively fast

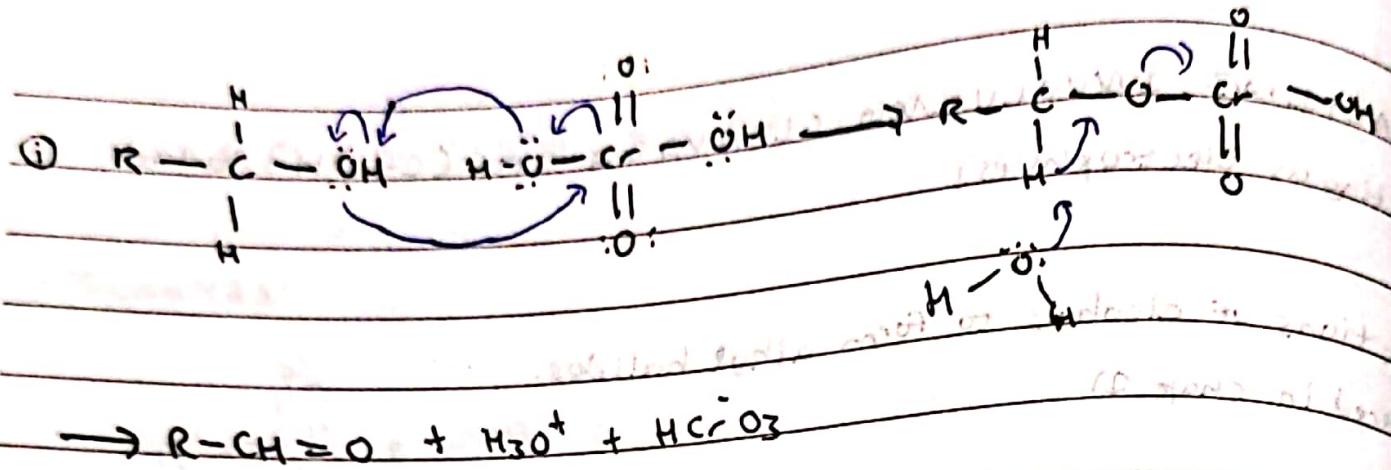


To drive the equilibrium to the right ethene is removed as it is formed.

(c) Oxidation

There are two types of oxidations possible for alcohols: Complete & partial oxidation.

Strong oxidizing agents can convert alcohols directly to ketones and then to carboxylic acids directly. Weaker oxidizing agents can only oxidize them up to aldehydes/ketones.



Oxidation mechanism's can be different for different oxidizing agents. But most of them follow this core process.

- **ACTIVATING OXIDANT:** Reaction takes place to make the oxidant more active.

Ex: Acid converts $\text{K}_2\text{Cr}_2\text{O}_7$ to H_2CrO_4 .

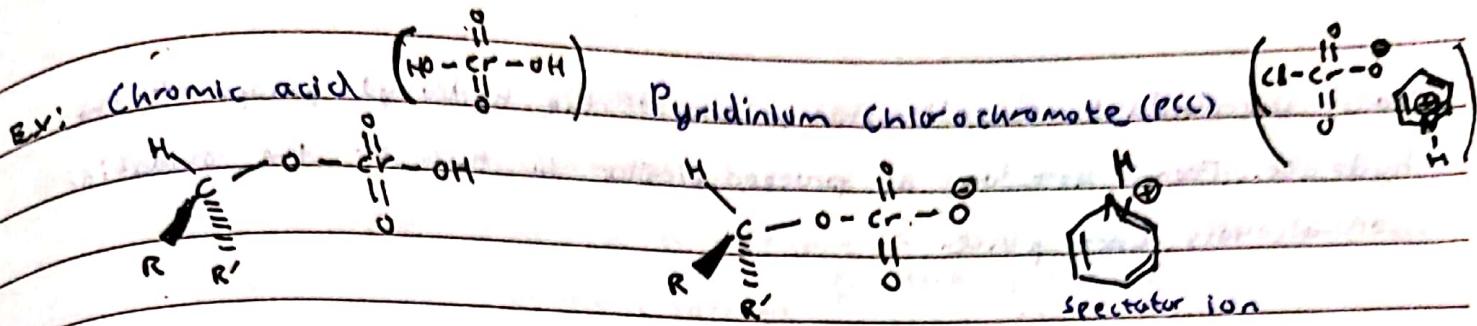
- **COORDINATION OF ALCOHOL TO OXIDANT:** This helps install a good leaving group on the oxygen atom. This is followed by proton transfer.

- **GLORIFIED ELIMINATION TAKES PLACE:** (-H bond is broken, good leaving group leaves, R-C-O (II) bond is formed.)

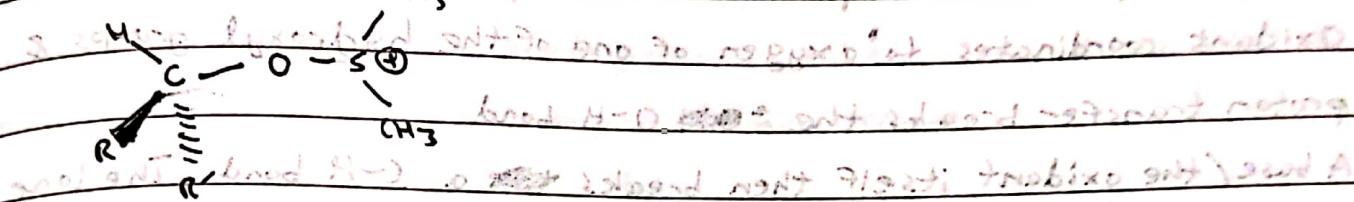
SUMMARY: In a series of reactions, the role of oxidizing agent is to

Here's what oxidants do :

- They coordinate to oxygen, and a proton transfer breaks the O-H bond.
- The atom coordinated to oxygen functions as a good leaving group.
- A base, ~~them~~, the oxidant itself then breaks the (-H bond), and the lone pair left repels and causes the leaving group to leave. O^- and then it forms the C-O (II) bond.



Swern Oxidation: Formation of carbonyl group at carbons 2,3 with overall loss of CH_3OH

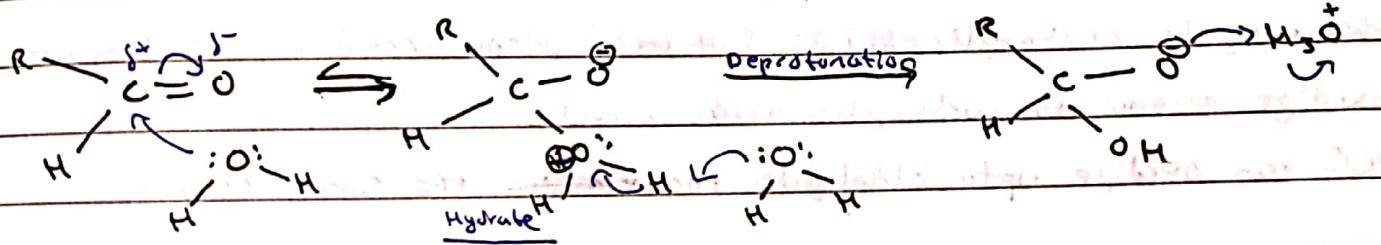


This is for oxidation of alcohols to ketones. Using 2 equivalents of reagent

OXIDATION OF ~~ALCOHOLS~~ ALDEHYDES TO CARBOXYLIC ACIDS

The exact same mechanism does not occur here. This is because any species basic enough to remove H_{C}^+ , i.e., break the C-H bond is more likely to add to carbon. This is because the $\text{C}=\text{O}^+$ carbon is very electrophilic. ($\text{C}^{\oplus}=\text{O}^{\ominus}$)

However, again, for the majority of oxidants, a similar mechanism takes place. With the involvement of water this time since ($\text{C}^{\oplus}=\text{O}^{\ominus}$) the C is electrophilic, water adds to it.



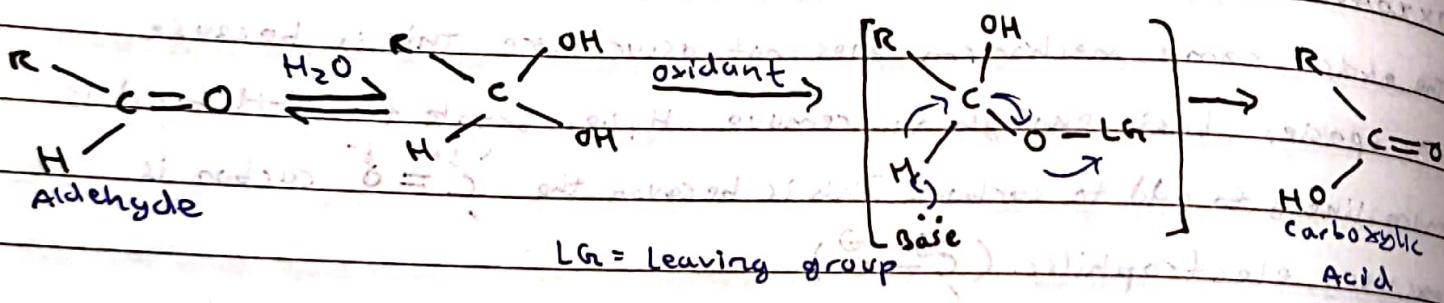
Protonation at the hydrate formed gets deprotonated and then protonated to attain more stability. H^+

Lorillard records literature entries mention precision across a pH of 900%.

Now, the oxidant co-ordinates to one of the hydroxyl groups of the hydrate. From here on, a process similar to that of the oxidation of alcohols takes place.

- Water attacks aldehyde to form hydrate. Attains increased stability through deprotonation & protonation to possess a hydroxyl (OH) group
- Oxidant coordinates to oxygen of one of the hydroxyl groups & proton transfer breaks the $\text{O}-\text{H}$ bond
- A base / the oxidant itself then breaks ~~a~~ a $\text{C}-\text{H}$ bond. The lone pair left produces repulsions which causes the leaving group to leave.

This is followed by formation of the $(-\text{O}(\text{II})\text{O}-)$ bond.

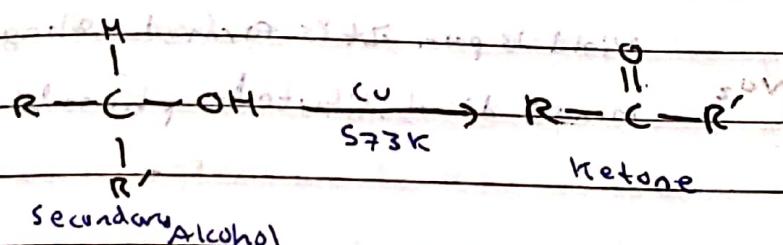
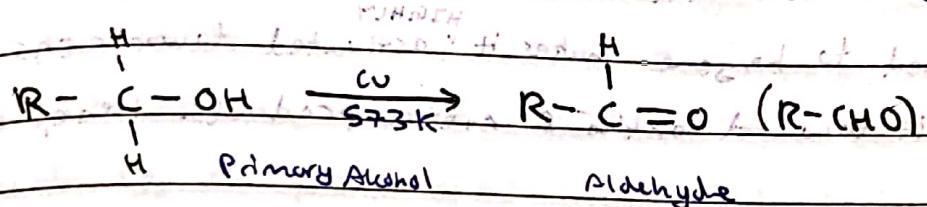


- * Oxidants like $\text{Cr}_2\text{O}_7^{2-}$ ~~exist~~ in anhydrous medium oxidises aldehydes to ketones. But due to lack of water, it cannot oxidise from all the way to carboxylic acids. But in hydrous medium $\text{Cr}_2\text{O}_7^{2-}$ can oxidize alcohols to carboxylic acids directly.
- * PCC can oxidize upto aldehydes for ~~the same reason~~ the same reason.

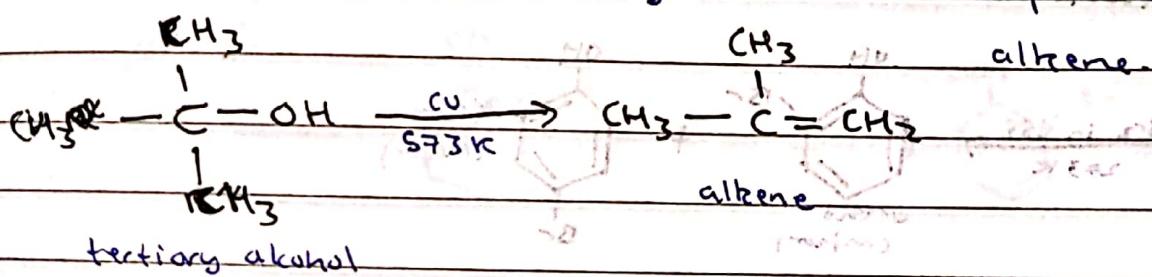
- * Ketones cannot be further oxidized due to lack of a removable $-\text{H}$ group on C. Hence no π bond can be formed on the ketone hydrate.
- * Due to this same reason, tertiary ~~alcohols~~ alcohols cannot be oxidized.

However, in the presence of extremely strong oxidising agents like KMnO_4 at elevated temperatures, destructive oxidation takes place. (Cleavage of C-C bond occurs & a mixture of carboxylic acids containing lesser number of carbon atoms is formed) (For tertiary alcohols)

+ When vapours of a primary or secondary alcohol are passed over heated copper at 573K , dehydrogenation takes place & an aldehyde (primary alk) or ketone (secondary alc.) are formed.



When vapours of a tertiary alcohol is passed over heated copper at 573K , dehydrogenation dehydration takes place to produce an

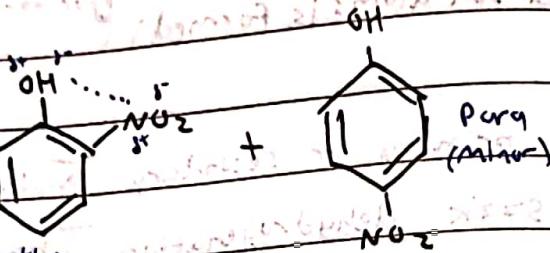
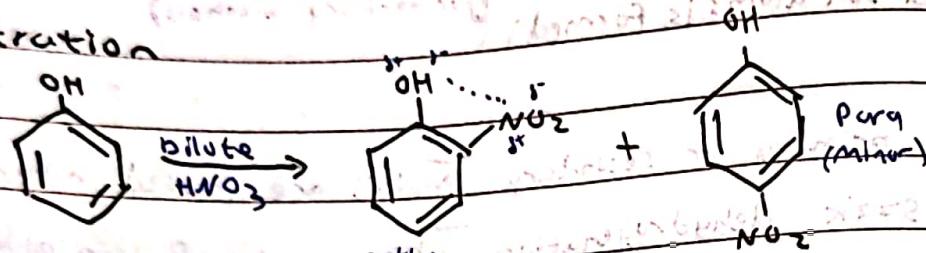


*Oxidation of alcohols generally takes place with alkaline KMnO_4 instead of acidified KMnO_4 even though acidified KMnO_4 is a much more powerful oxidising agent because acidified KMnO_4 can char and oxidize alcohols all the way to CO_2

REACTIONS OF PHENOLS

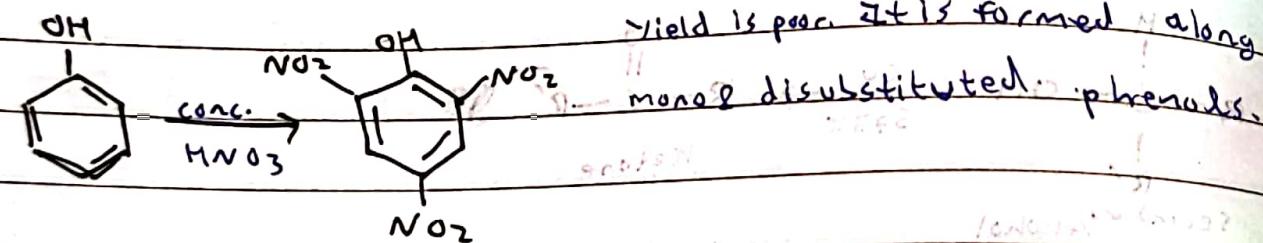
(i) EAS REACTION

(a) Nitration

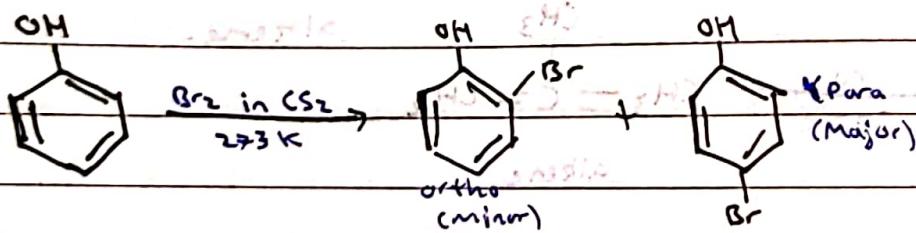


Due to intramolecular hydrogen bonding

The -OH group attached to benzene makes it highly activated towards reaction & directs it toward ortho & meta products.

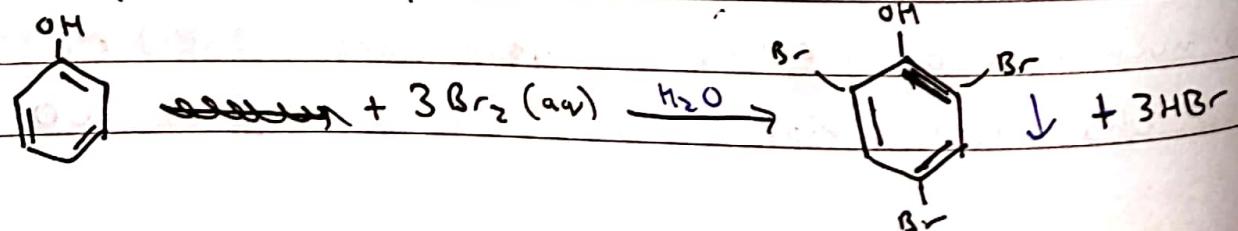


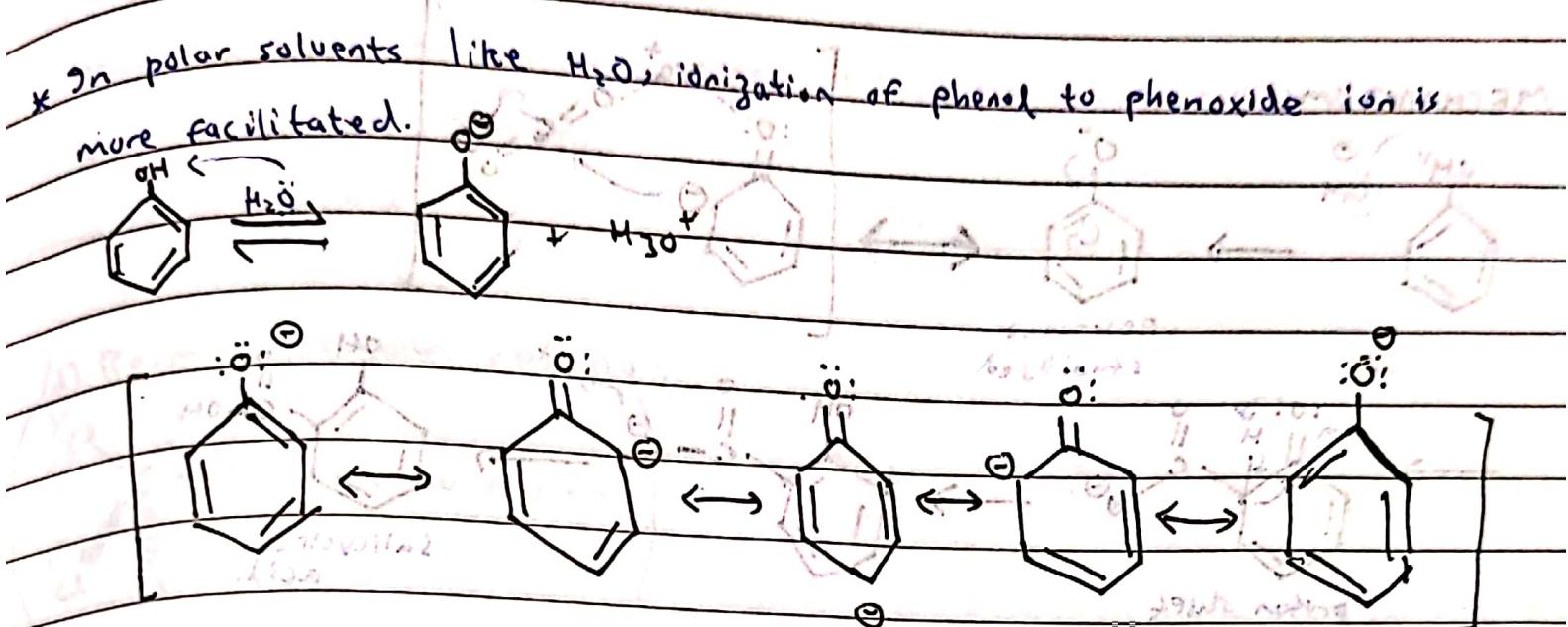
(b) Halogenation



In non-polar solvents like CS_2 & CCl_4 , mono substituted products are formed, at low temperatures.

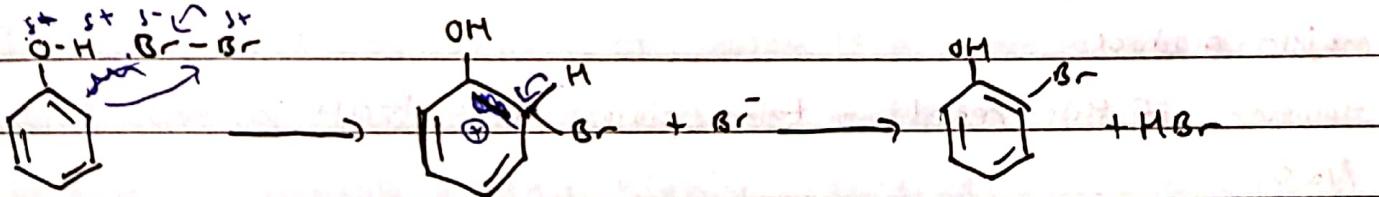
In polar solvents,



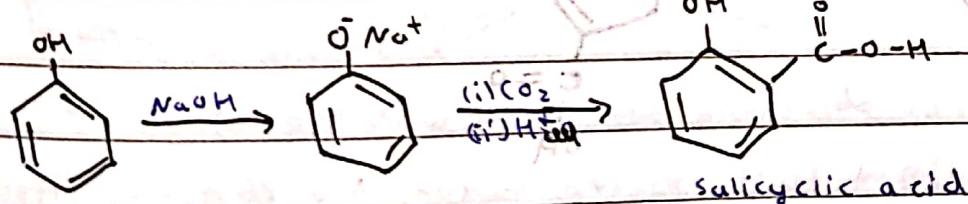


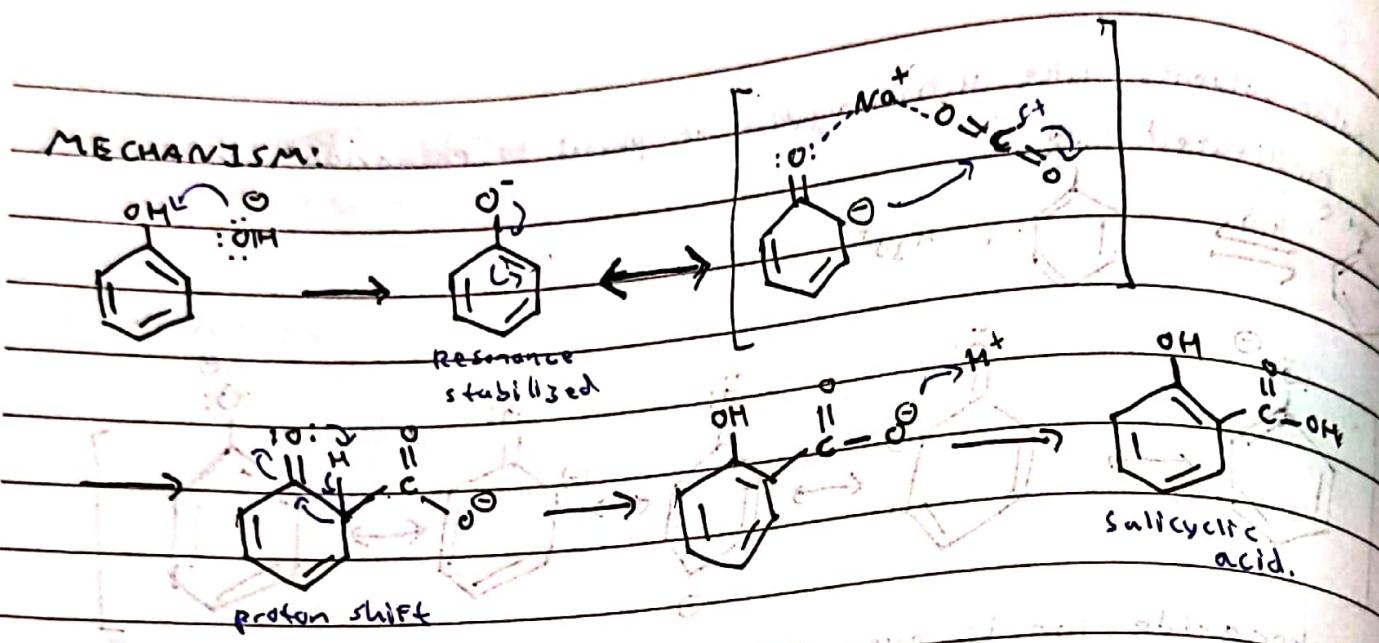
The phenoxide ion is even more highly activating than phenol. Further, the bromonium ions formed are stabilized ~~due to~~ in polar medium. All this facilitates EAS & hence tri-substituted product is formed in polar solvent.

* Generally, halogenation is carried out in the presence of a Lewis acid, like Fe Br_3 which helps produce Br^+ ions. However, with phenols, even in the absence of a Lewis acid, due to higher activated ring & polarisation of O-H bond, halogenation occurs.



(a) KOLBE'S REACTION





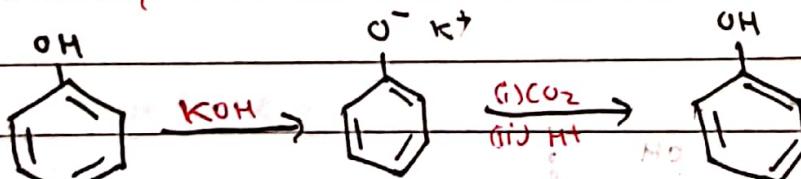
JEE NOTES

$$Na^+ \rightarrow 0.95 \text{ \AA} \quad \left. \begin{array}{l} \text{radii} \\ \text{of cations} \end{array} \right\}$$

$$K^+ \rightarrow 1.33 \text{ \AA} \quad \left. \begin{array}{l} \text{radii} \\ \text{of anions} \end{array} \right\}$$

* Na⁺ serves as an anchor & guides CO₂ to the ortho position during the formation of the intermediate. Na⁺ is chelated, i.e., forms coordinate bonds with phenoxide & CO₂, temporarily. Hence it directs the reaction in the ortho direction & ortho is major product.

* However, if this reaction takes place with KOH instead of NaOH,



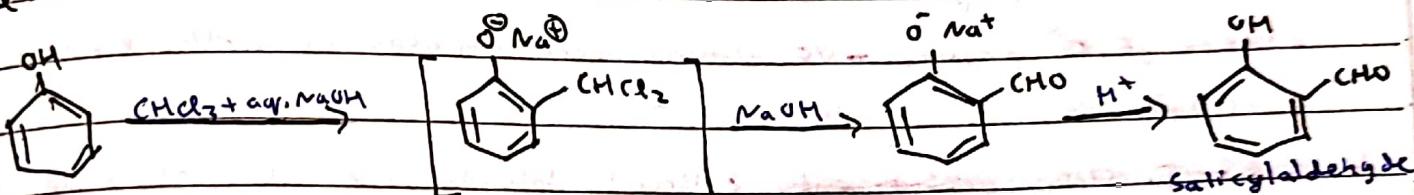
4-hydroxy benzoic acid. This is because with the bigger K⁺ ion, the chelating effect

is not possible.

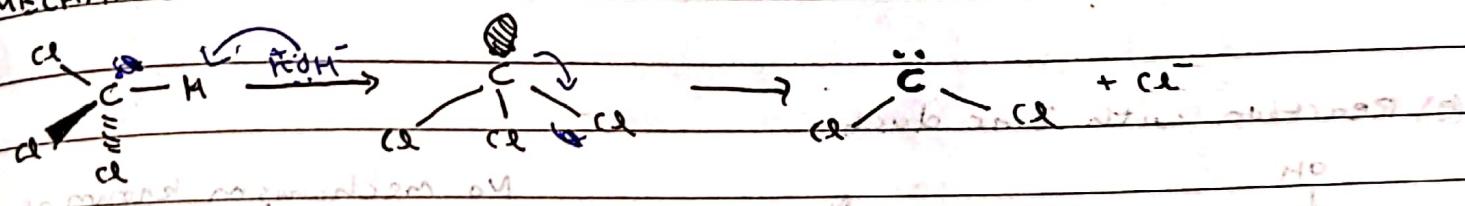
* Although, due to no chelation both products are minimum

Hence the usual para-directing effect of EAS reaction prevails & para product is major product.

(d) Reimer-Tiemann reaction



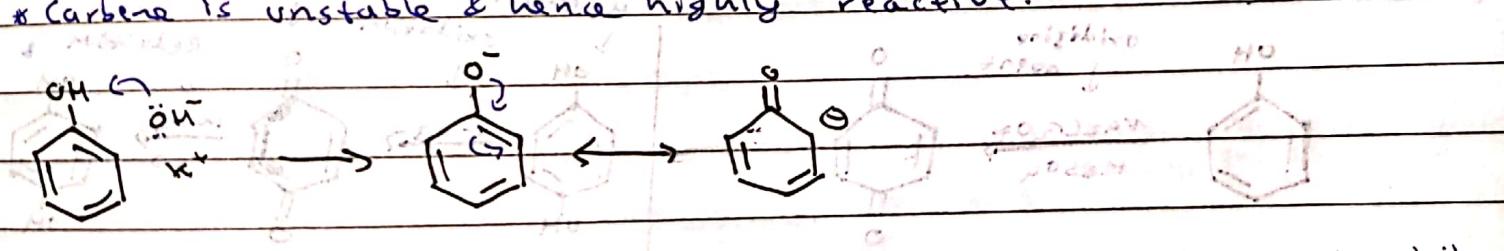
MECHANISM:



* The strongly basic aqueous NaOH solution deprotonates chloroform.

The lone pair on C repels Cl, which is a good leaving group to leave, forming the dichloro carbene ~~resonance~~ anion.

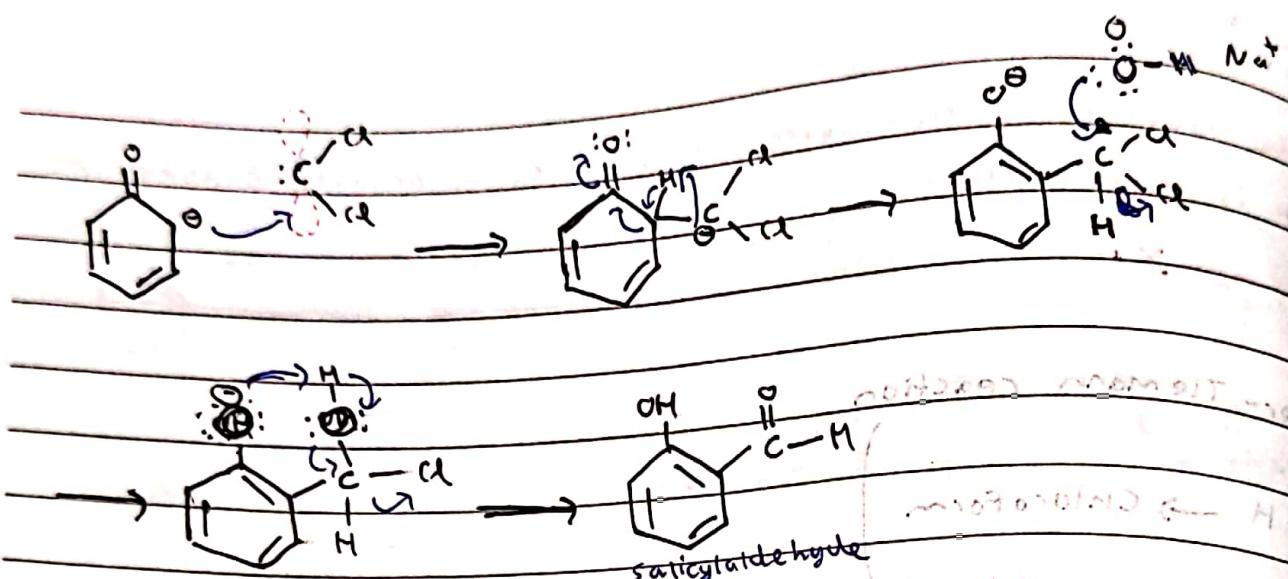
* Carbene is unstable & hence highly reactive.



sp^2 hybridised
empty p-orbital

Hence, the phenoxide ion acts as a nucleophile and attacks the empty p-orbital in dichloro carbene.

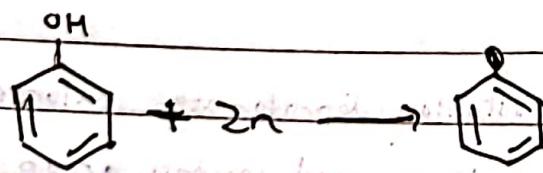
S_N2 mechanism



* In this reaction, phenoxide acts as a nucleophile. Due to +R effect of O^- group, -ve charge accumulates on ortho & para positions.

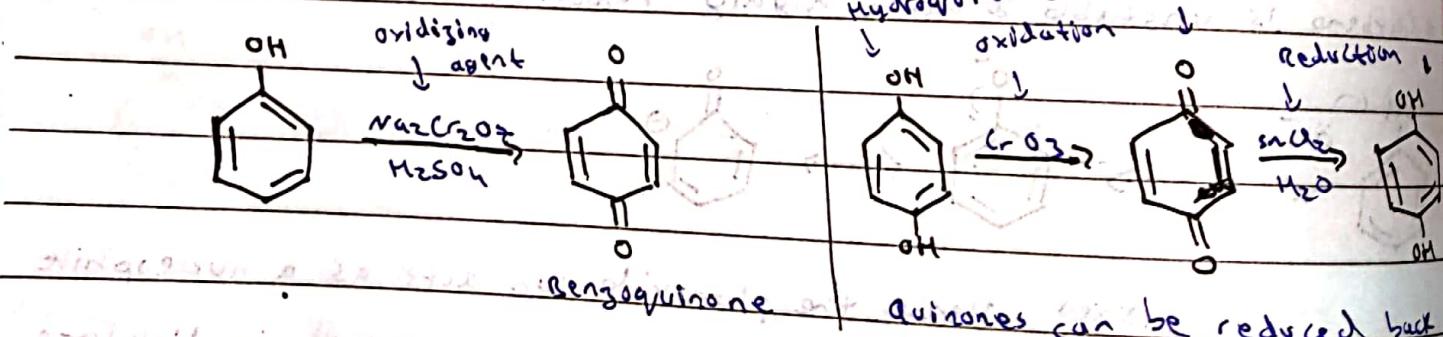
* Further, ~~salicylaldehyde~~ exhibits intramolecular hydrogen bonding and hence is more stable than para-hydroxy benzaldehyde. Hence ortho product is major product.

(E) Reaction with zinc dust.

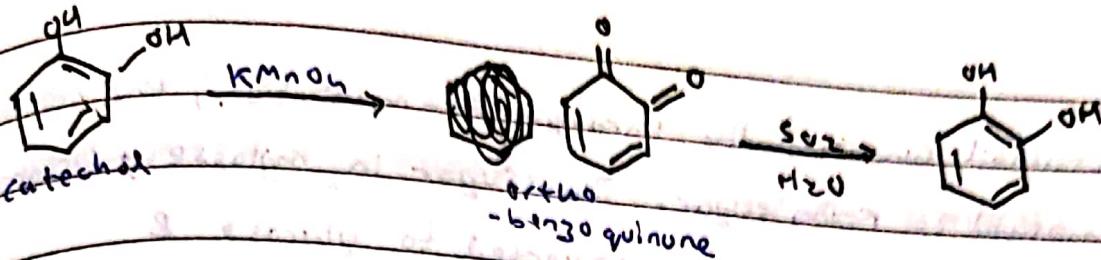


No mechanism known as

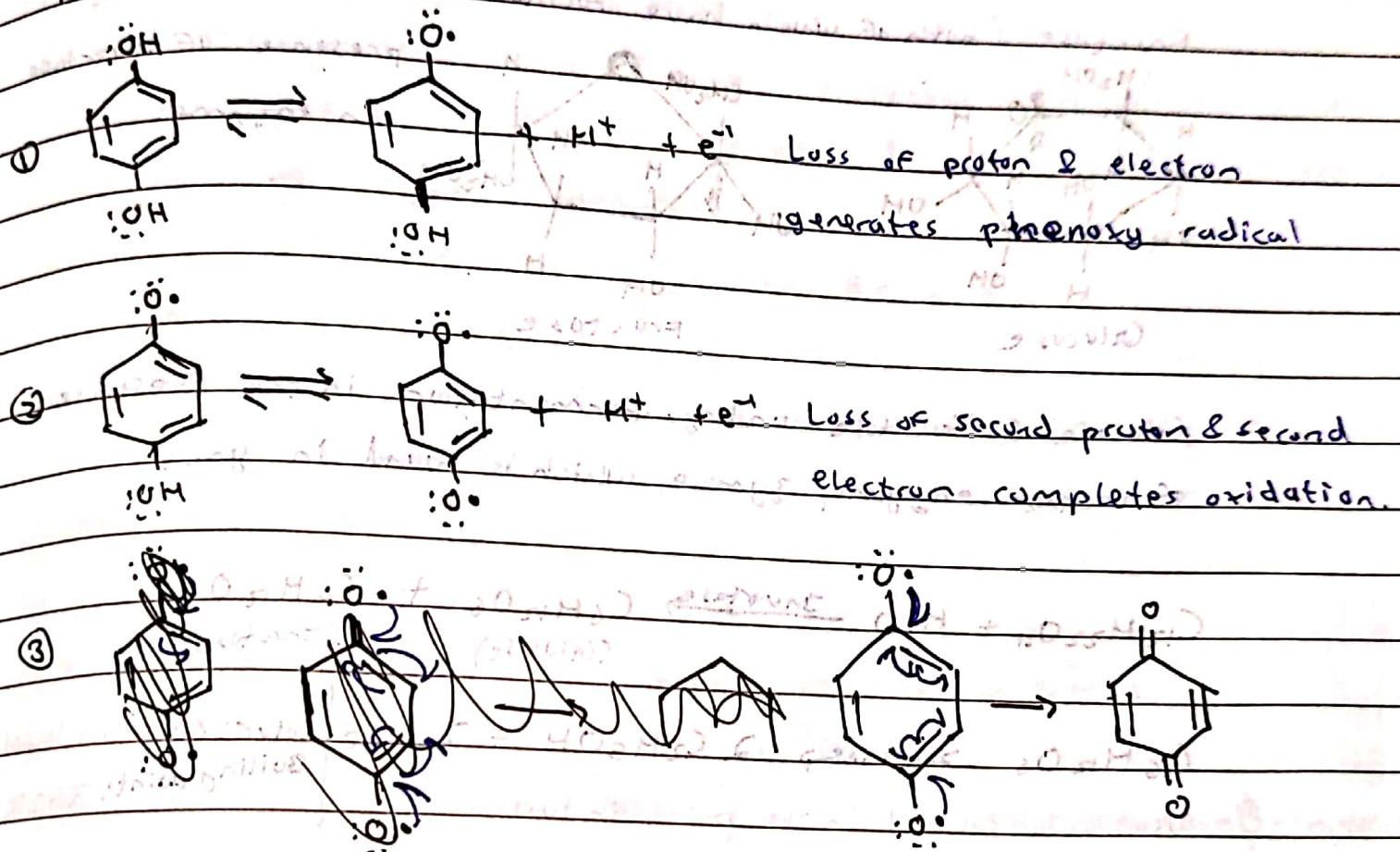
(F) Oxidation.



Quinones can be reduced back to the hydroquinone

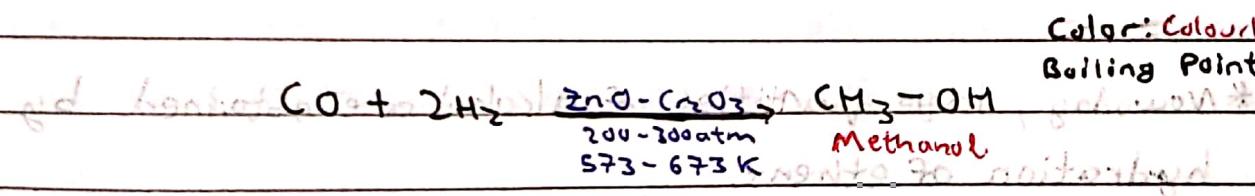


MECHANISM:



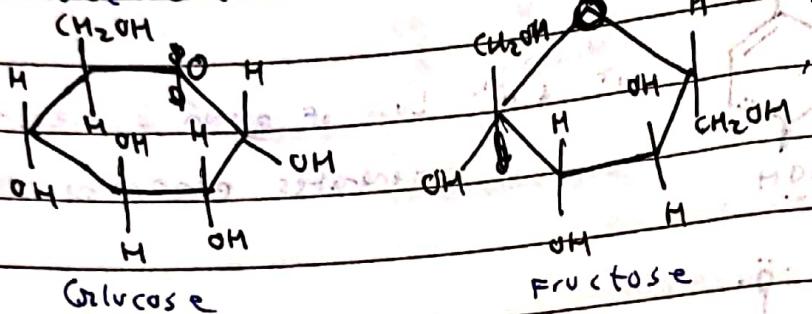
~~C~~ COMMERCIAL METHODS FOR PRODUCTION OF ALCOHOLS

- **METHANOL:** Produced by catalytic hydrogenation of carbon monoxide at high temp. & high pressure in the presence of $\text{ZnO-Cr}_2\text{O}_3$ catalyst.

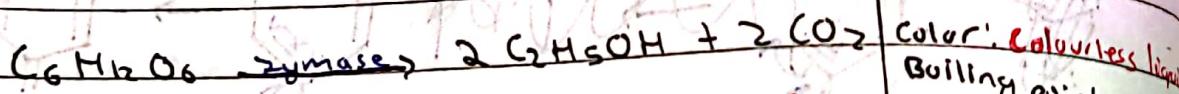
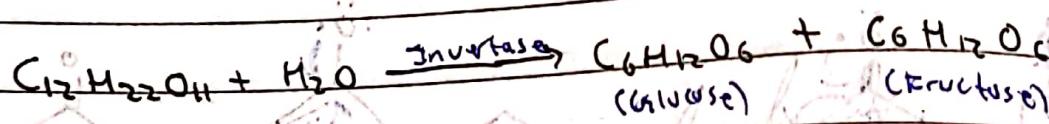


Poisonous in nature. Can cause blindness & in large quantities, death.

Used as solvent in paints, varnishes & chiefly for making formaldehyde ($\text{H}-\text{CHO}$)



Glucose & Fructose undergo fermentation in the presence of another enzyme, zymase, which is found in yeast.



Used as a solvent in the paint industry

in the preparation of numerous carbon compounds.

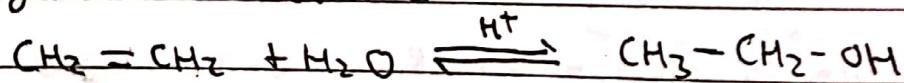
DENATURATION OF ALCOHOL: The commercial alcohol is

made unfit for drinking by mixing it in some copper

Sulphate (to give it color) & pyridine (foul smelling liquid)

This is known as denaturation of alcohol.

* Nowadays, large quantities of alcohol are obtained by hydration of ethene

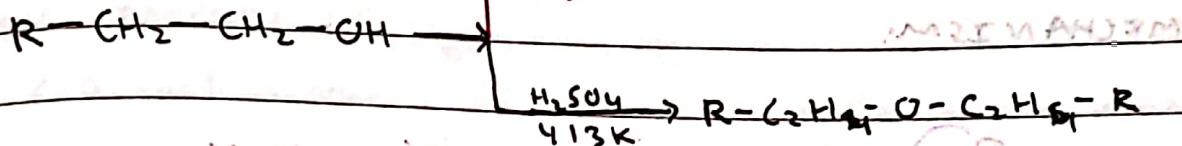


ETHERS:

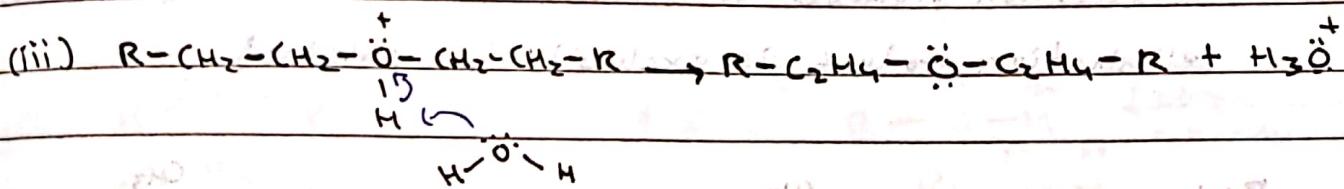
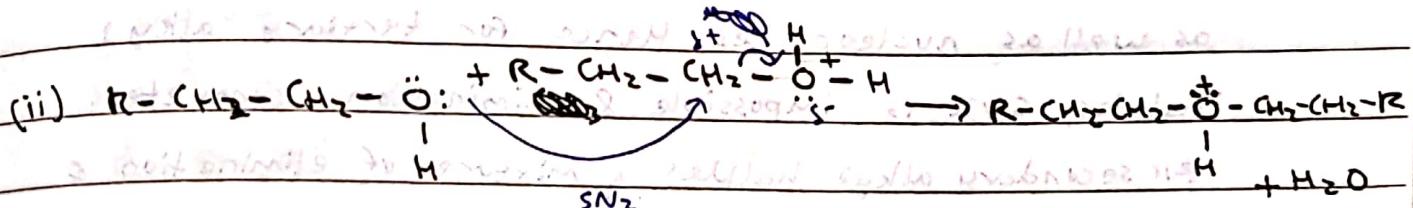
MECHANISMS FOR PREPARATION OF ETHERS

(a) By dehydration of alcohols

Alcohols undergo dehydration in the presence of protic acids to produce either alkenes or ethers. The reaction product depends upon the reaction conditions.



MECHANISM:



The formation of ethers is a nucleophilic bimolecular reaction

i.e., SN2 involving the attack of alcohol molecule on a protonated alcohol.

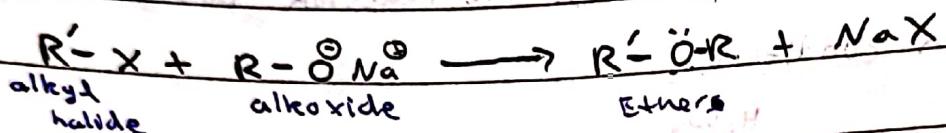
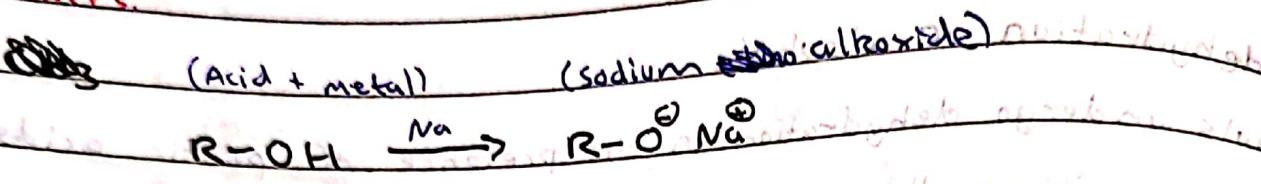
* Only symmetric ethers can be prepared via this method.

* Temperature must be kept low or reaction will prefer Sv1 & produce alkenes.

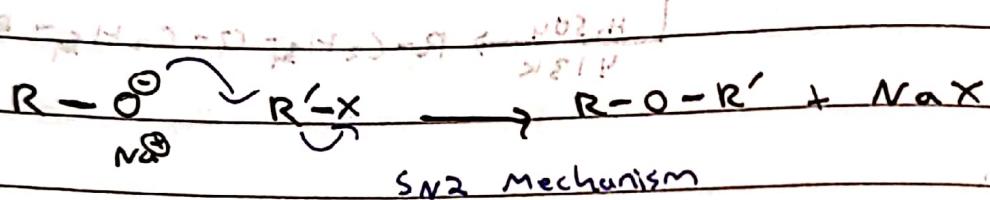
* only suitable for primary alcohols. For secondary & tertiary alcohols, both Sv1 & elimination take priority & hence form alkenes.

1 (b) WILLIAMS ONE SYNTHESIS.

WILLIAMSON'S SYNTHESIS.
It can be used for preparation of both symmetrical & unsymmetrical ethers.



MECHANISM.

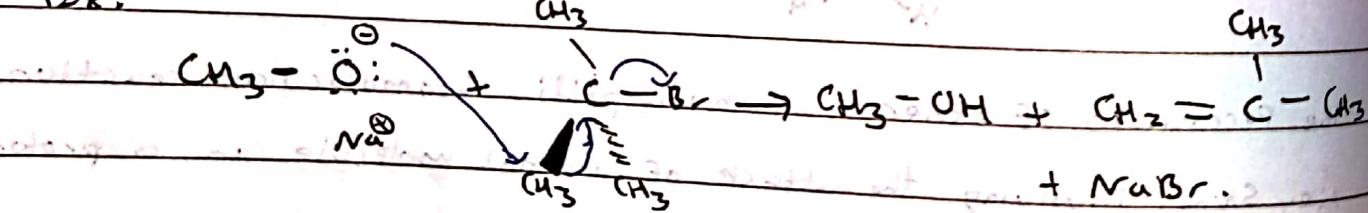


* Note: This reaction works best with primary alkyl halides. This is because alkoxides ($\text{R}-\text{O}^-$) are both strong bases as well as nucleophiles. Hence for tertiary alkyl halides, $\text{S}_{\text{N}}2$ is impossible & elimination competes.

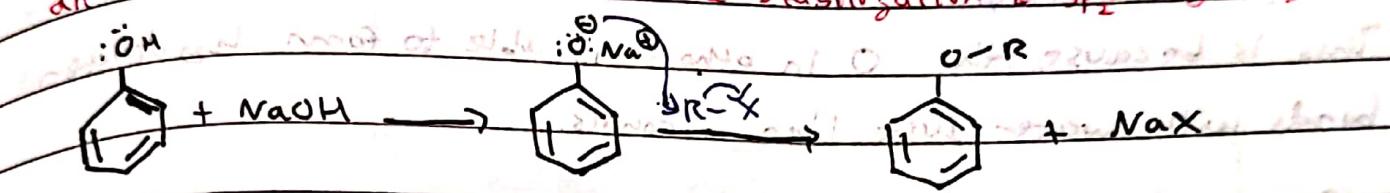
For secondary alkyl halides a mixture of elimination & substitution products will be formed. For tertiary halide

elimination product is exclusively obtained.

Ex:



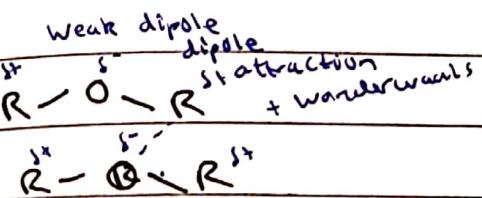
* Phenols are also converted to ethers by this method.
Here, phenols are converted to phenoxide to act as the nucleophile. This is because it is much more difficult to break the $C-X$ bond on an aromatic carbon due to resonance stabilization & sp^2 hybridization.



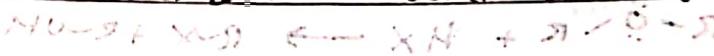
PHYSICAL PROPERTIES

(BOILING POINT)

* The C-O bond in ethers are mildly polar & thus have a small / weak net dipole moment. This weak polarity does not appreciably affect their boiling points. Their B.P.'s are comparable to that of alkanes of similar molecular masses & much lower than that of alcohols.

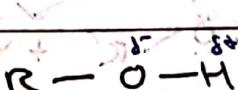
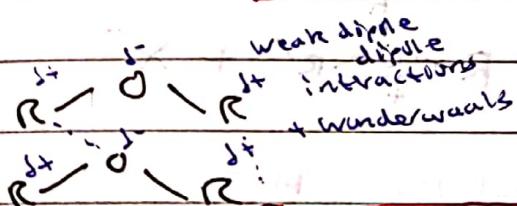


only van der waals forces



INTERACTION

SIMILAR BOILING POINTS



strong

Hydrogen bonding + van der waals



ALCOHOLS HAVE MUCH HIGHER B.P.

Intermolecular forces are called as London or 'L' forces

and they are responsible for non-polar liquids not miscible with water

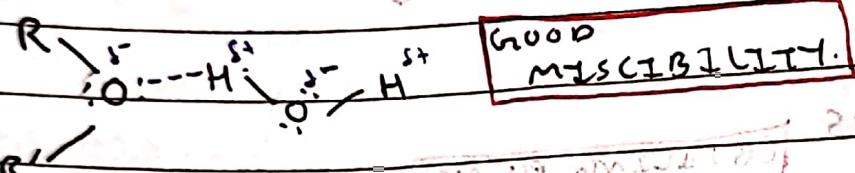
giving rise to branched chain and branched molecules

* MISCELLIBILITY

The miscibility of ethers "resembles that of alcohols." in water.

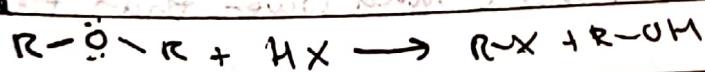
To be miscible, the bonds between the 2 liquids must be as strong as or stronger than the bonds between itself.

This is because the O in ethers is able to form hydrogen bonds with water just like alcohols.



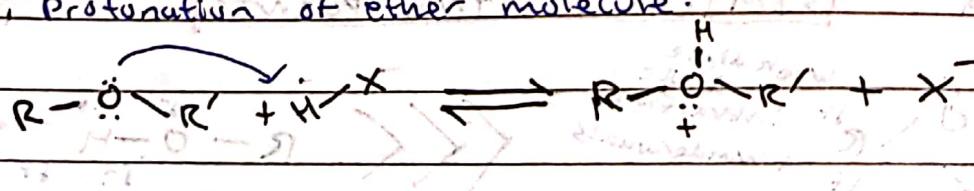
CHEMICAL REACTIONS OF ETHERS

(a) Cleavage of C-O bond in ethers



Mechanism:

Step 1: Protonation of ether molecule.

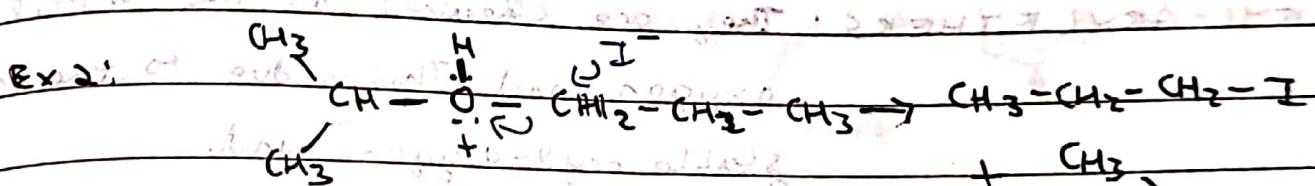
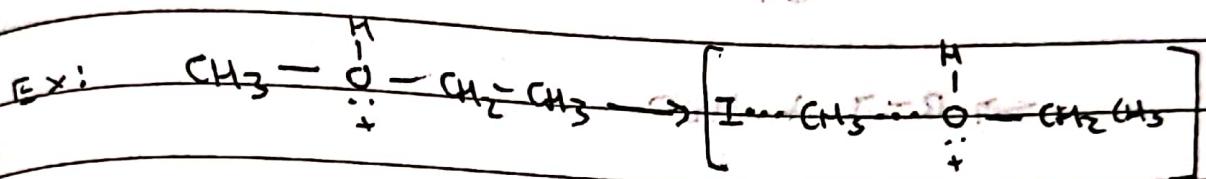


Order of reactivity of hydrogen halides is $H-I > H-Br > H-Cl$

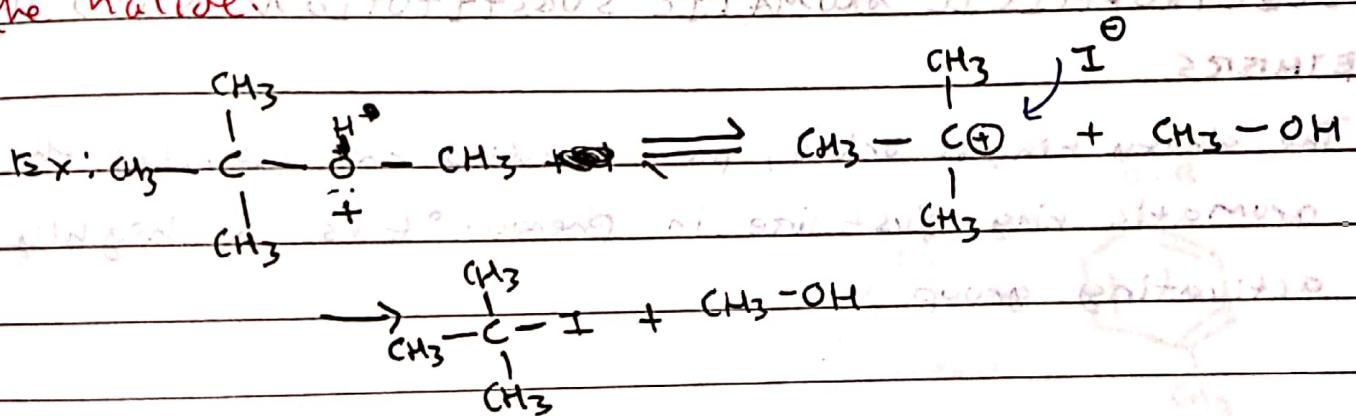
Cleavage of ethers takes place with $H-I & H-Br$ at high temperature.

Step 2: An alcohol & a halide are formed. For unsymmetric ethers the hydrocarbon group that forms the alcohol & the one that forms the halide depend on the following.

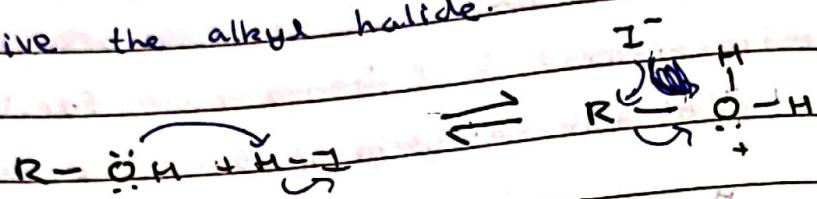
* FOR PRIMARY (1°) & SECONDARY (2°) ETHERS: X^- , let us assume is iodide, is a good nucleophile & hence will attack the least substituted carbon. This is because it is the carbon with least steric hindrance around it & hence more facilitating for S_N2 attack. The lower alkyl group forms the halide.



* FOR TERTIARY (3°) ETHERS: If one of the alkyl groups are tertiary, the carbocation formed by removal of leaving group is very stable & hence tends to undergo S_N1 mechanism. Hence the tertiary alkyl group, i.e; the most substituted carbon is attacked by the X^- nucleophile & forms the halide.



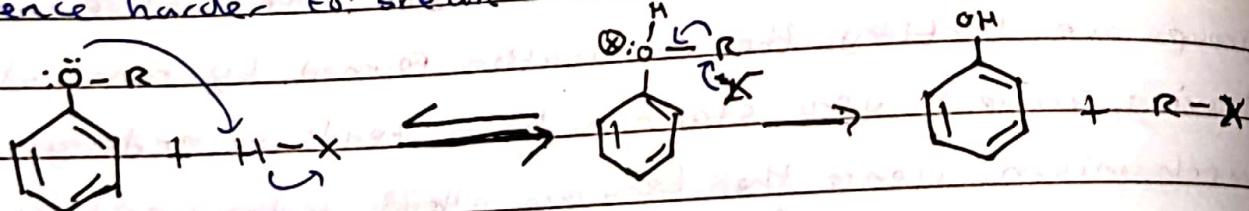
Step 3: If $H-X$ is in excess & reaction is carried out at high temperatures, the alcohol reacts with $H-X$ to give the alkyl halide.



* ARYL ETHERS

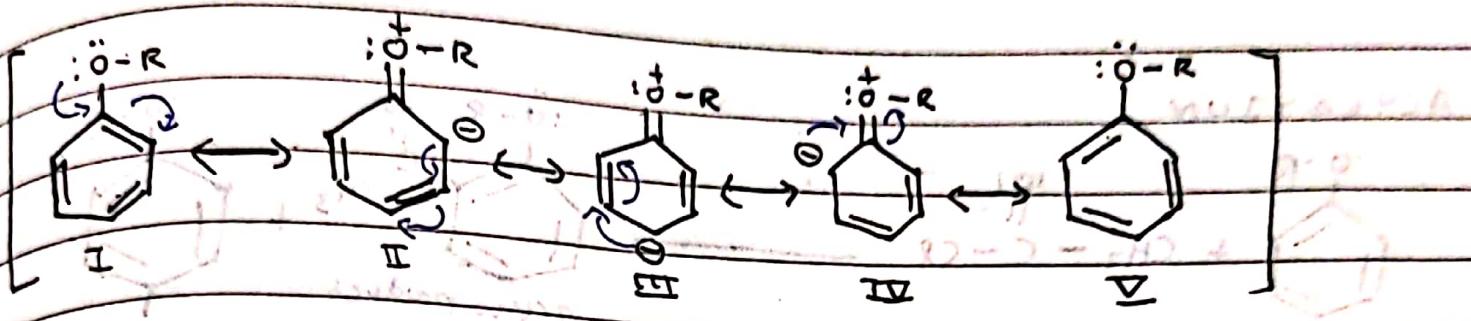
* ALKYL-ARYL ETHERS: They are cleaved at the alkyl-oxygen bond. This is due to the more stable aryl-oxygen bond.

+ The aryl oxygen bond O has partial double bond character & the carbon forms sp^2 hybridized bonds which are stronger & hence harder to break than the alkyl-oxygen bond.



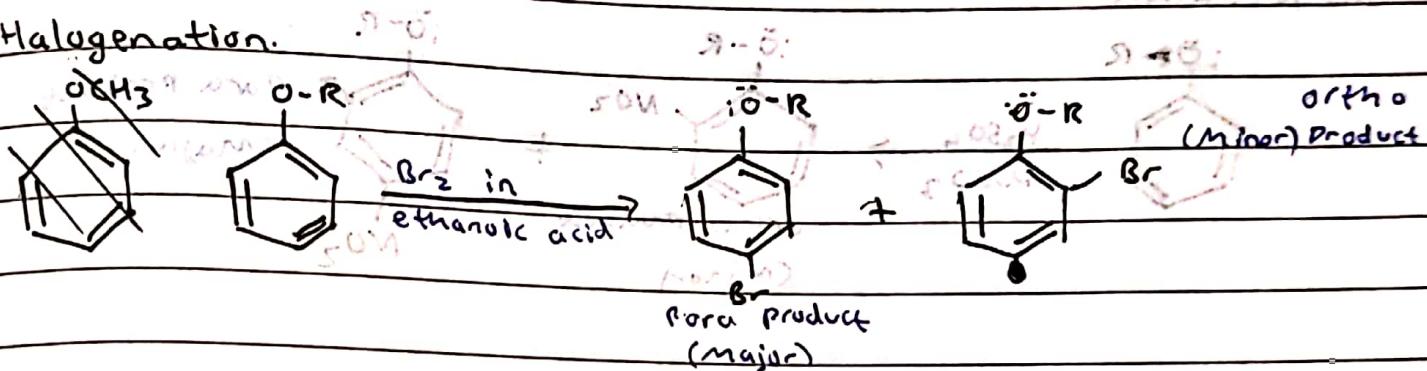
(b) ELECTROPHILIC AROMATIC SUBSTITUTION (EAS) OF ETHERS

The -alkoxy ring is ortho, para directing and activates the aromatic ring just like in phenols. It is a highly activating group.



Negative charge of resonating structure is on -ortho & -para positions.

(i) Halogenation.

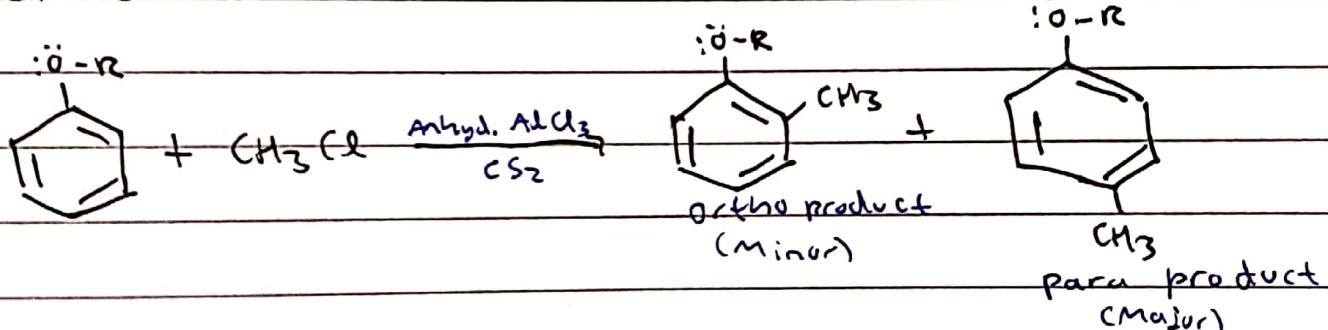


* The $\text{O}-\text{R}$ group makes the ring polar & hence it is only soluble in a slightly protic polar solvent like ethanolic acid which is also relatively inert enough to not react with Br_2 .

* The $\text{O}-\text{R}$ group causes the ring to be activated enough to attack Br_2 itself, even in the absence of catalysts like FeBr_3 .

(ii) Friedel-Crafts reactions:

ALKYLATION



ACYLATION



(iii) Nitration

