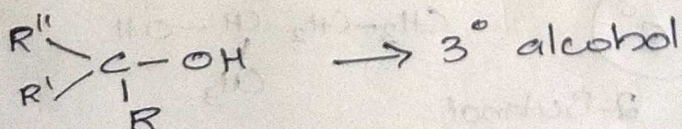
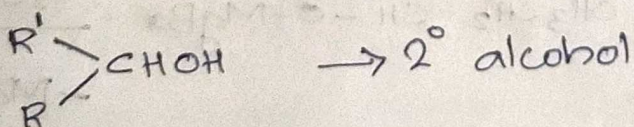


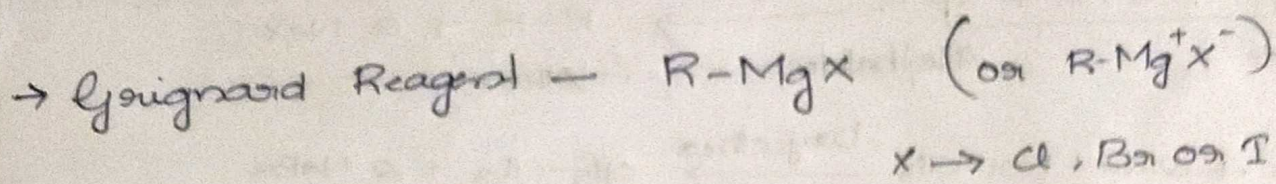
ALCOHOLS

→ Compound with general formula $R-OH$

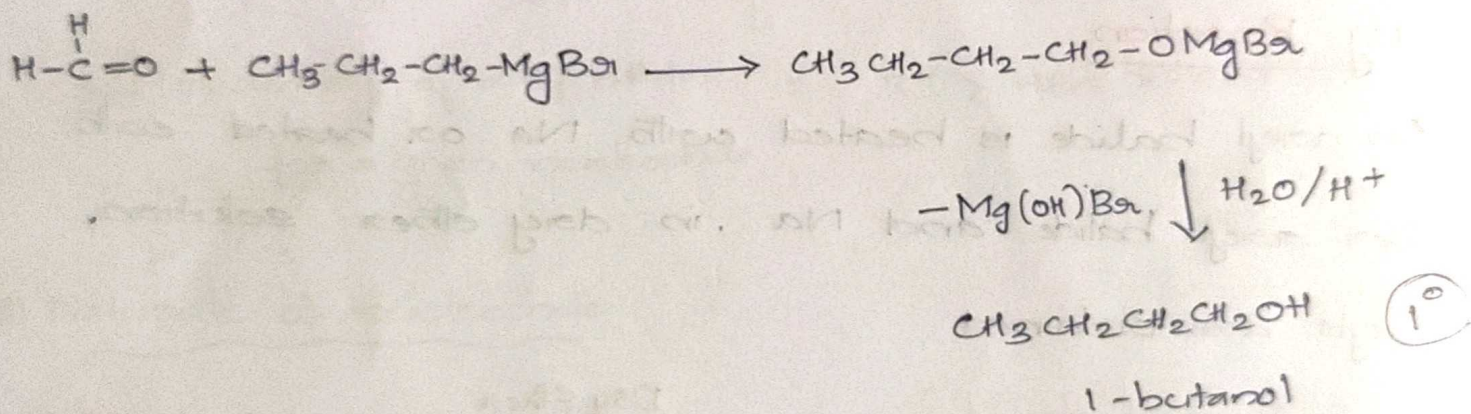
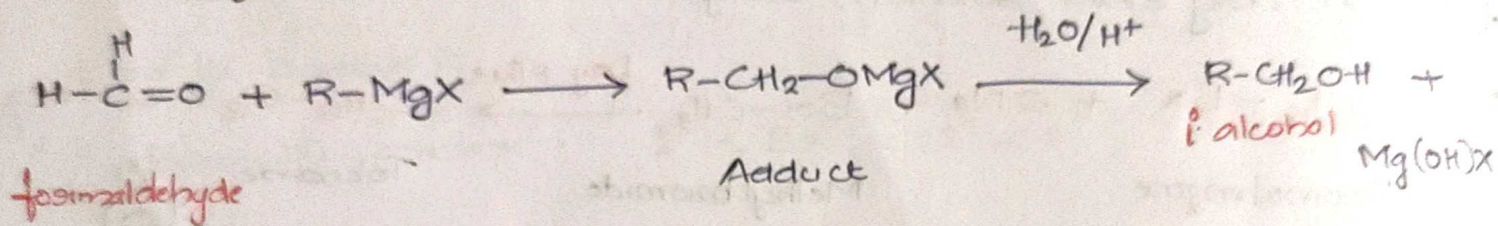
$R \rightarrow$ Alkyl / substituted alkyl
grp



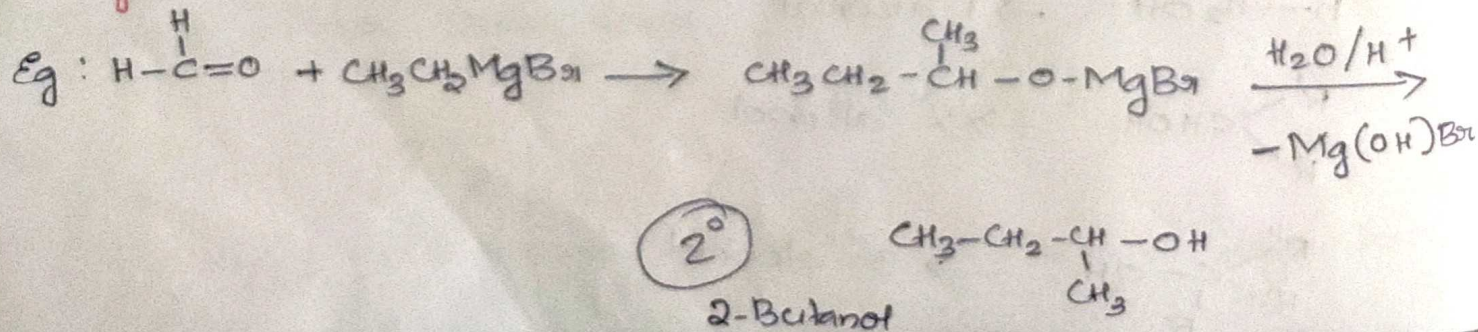
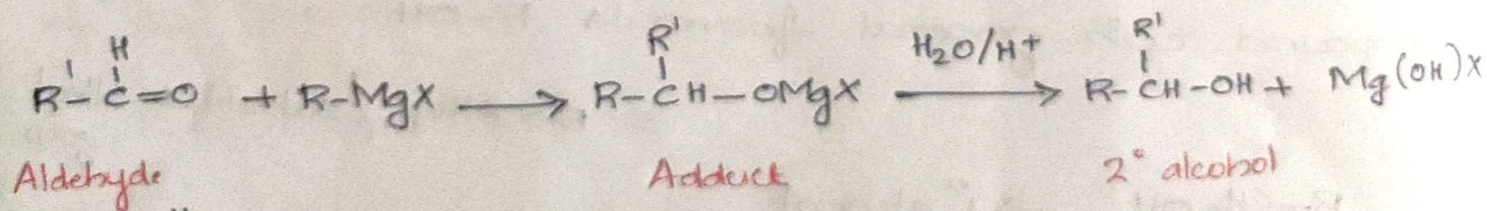
Preparation of alcohol from Grignard reagent



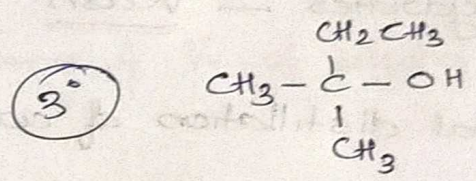
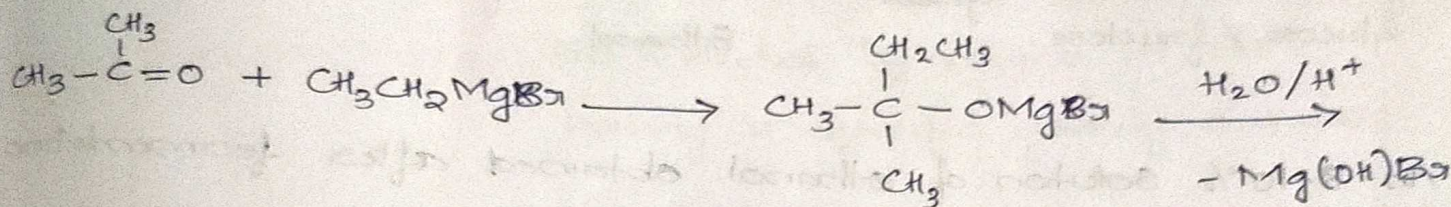
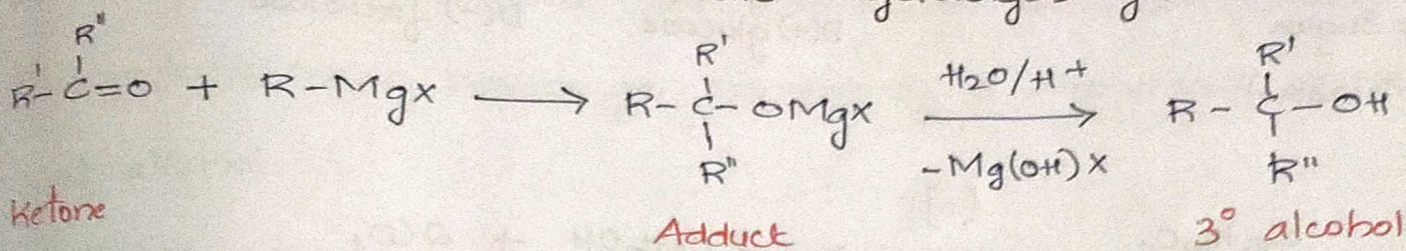
(A) Formaldehyde reacts with Grignard reagents to form addition product which on acidic hydrolysis gives primary alcohols.



(B) Aldehydes other than formaldehyde react with Grignard reagent to form addition products which on acidic hydrolysis give 2° alcohol



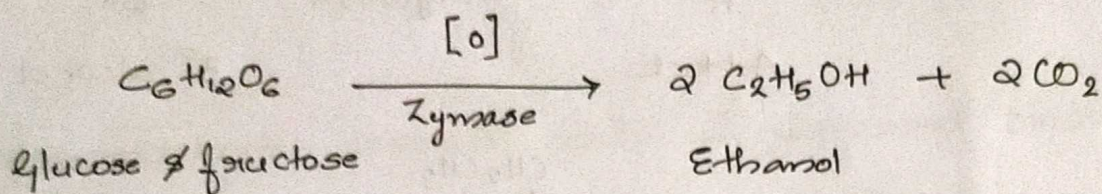
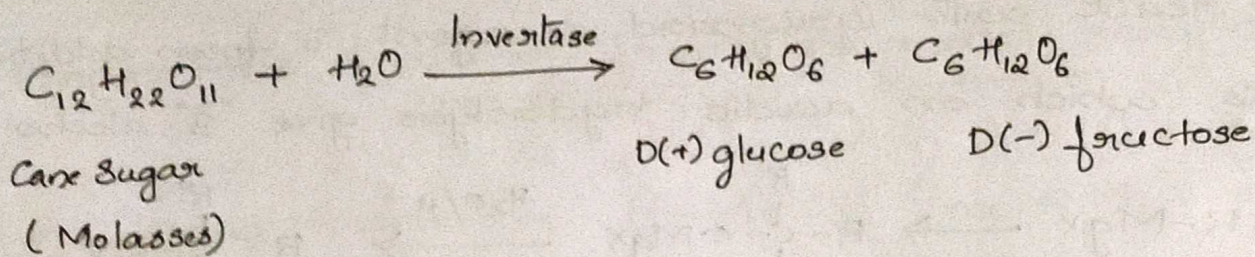
(c) Ketones react with Grignard reagent to form addition products which on acidic hydrolysis give 3° alcohol



2-methyl-2-butanol

Manufacture of ethanol from Molasses (preparation of "wash" and subsequent "rectified spirit" & "absolute alcohol")

- Ethanol is manufactured from molasses
- molasses — Mother liquor left after crystallisation of cane sugar & it contains ~40% uncrySTALLISABLE cane sugar.
- Molasses diluted with water to get 10% solution of sugar — Yeast is added to it & is kept at 303-308.K for 2-3 days — Enzyme invertase in yeast hydrolyse the sucrose into glucose & fructose — Enzyme zymase present in yeast convert both glucose & fructose into ethanol.



→ An 8-10% solution of ethanol obtained after fermentation of carbohydrates — Wash

→ Fractional distillation of wash give 95-6% solution of ethanol called rectified spirit

→ Distillation of rectified spirit over quick lime (CaO) & then over a few pieces of Calcium gives 100% ethanol known as absolute alcohol

Denaturation of alcohol — Denatured spirit

→ Alcohol for industrial purpose is rendered unfit for drinking by adding some $CuSO_4$ & poisonous / nauseating substance like methanol, pyridine etc — Process is called denaturation of alcohol / denatured spirit

→ Ethanol denatured with small quantity of methanol (5%) is called methylated spirit.

Proof Spirit

→ This term is used to represent an alcohol-water mixture or a beverage containing a standard amount of alcohol.

→ US : 100 proof - Mixture of H_2O & alcohol containing 50% alcohol by volume at $60^\circ F$ having a specific gravity 0.93353

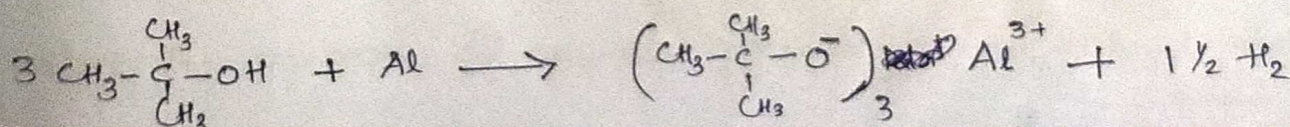
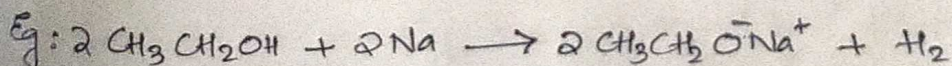
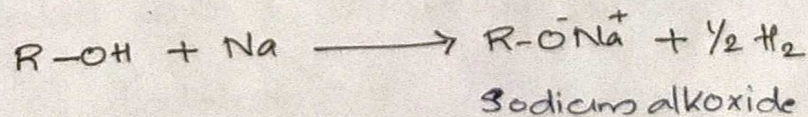
→ Nowadays the adopted mode is ~~not~~ stating alcohol content of beverages in terms of % of alcohol by volume (ABV) instead of proof.

Power alcohol

→ Ethanol is used as an additive to the fuels for automobiles or other internal combustion engines in certain countries; ethanol thus used for the generation of power is referred to as power alcohol.

Acidity of alcohols

→ Alcohols are feebly acidic - Illustrated by the fact that they react with active metals such as Na, K, Mg, Al etc to yield alkoxides

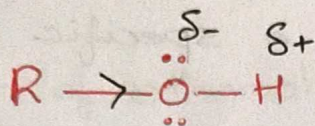


Explanation:

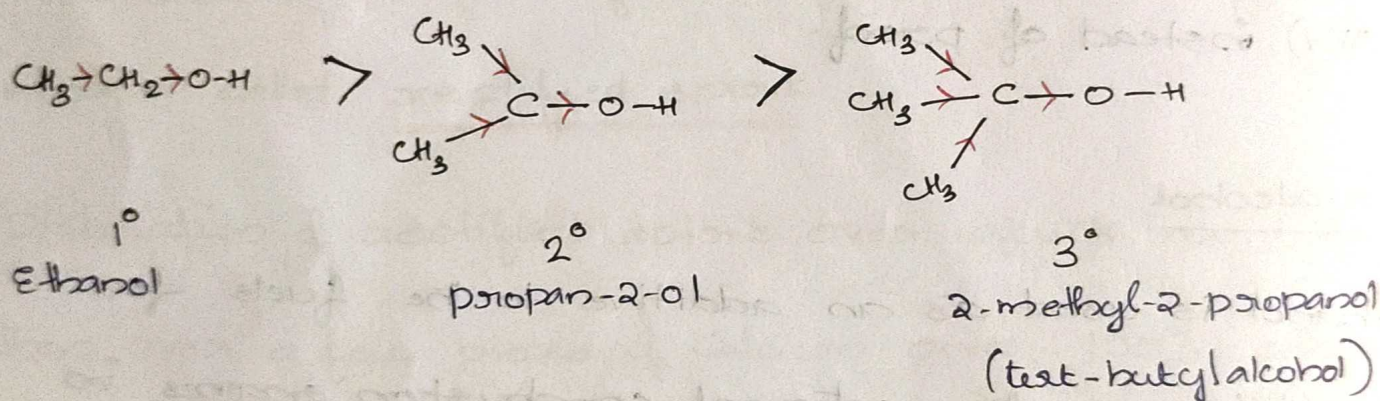
Order of acidity of 1°, 2° & 3° alcohols:

→ Acidic character of alcohol is due to the polar ^{nature} bond of O-H bond

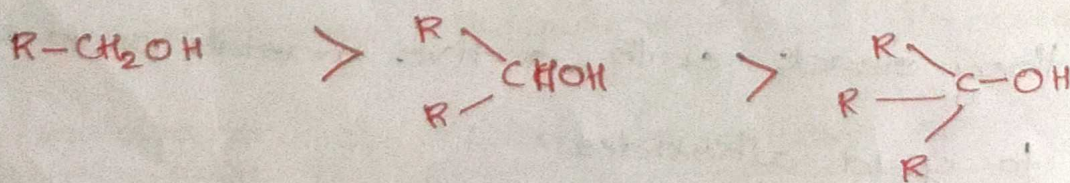
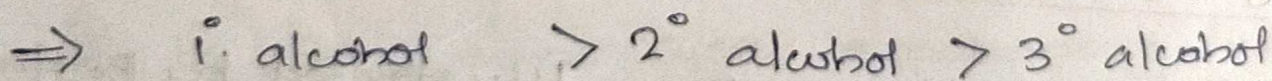
→ But are only weakly acidic because e⁻ releasing alkyl group increases the e⁻ density on oxygen by +I effect & consequently tend to decrease the polarity of O-H bond



This makes proton release more difficult & thereby decrease the acid strength.

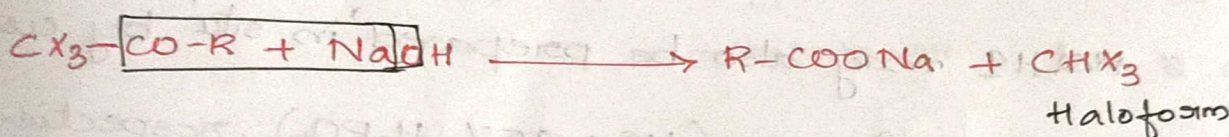
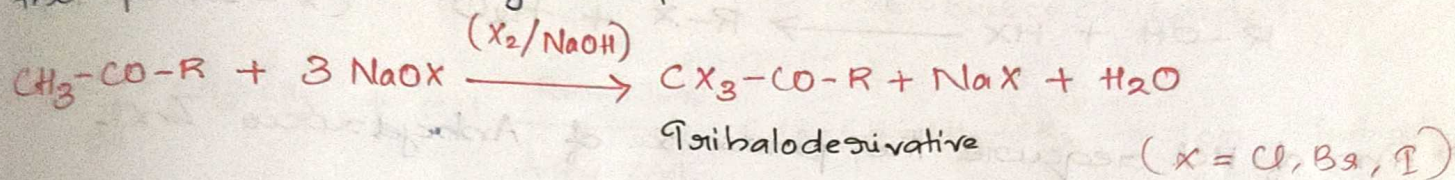


→ Greater no. of electron releasing alkyl group, greater will be decrease in the polarity of O-H bond due to their +I effect & lower will be the acidic character.

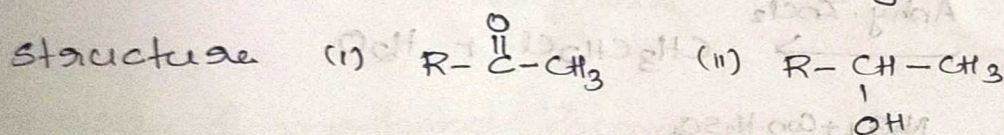


Haloform Reaction - Oxidation by hypohalite

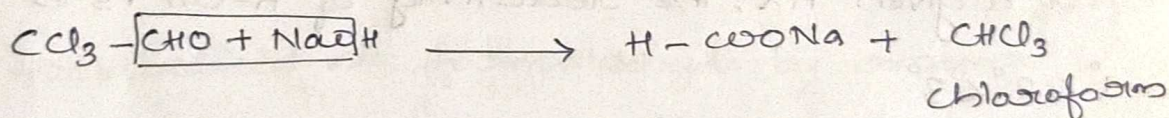
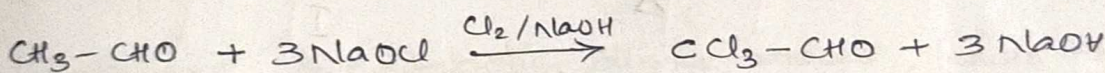
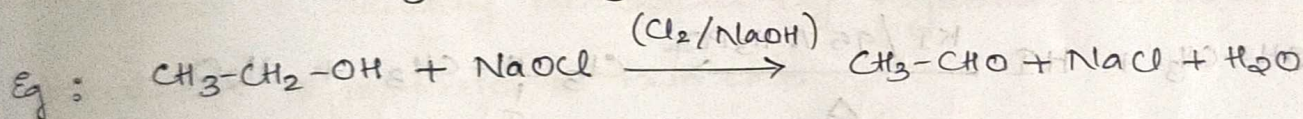
Acetaldehyde (CH_3CHO) & methyl ketones i.e. those which contain a $\text{CH}_3\text{CO}-$ grouping are oxidised by halogen & alkali result in the formation of haloform & the salt of carboxylic acid containing one carbon less than the parent carbonyl compound.



→ Haloform rxn is answered by any compound of the

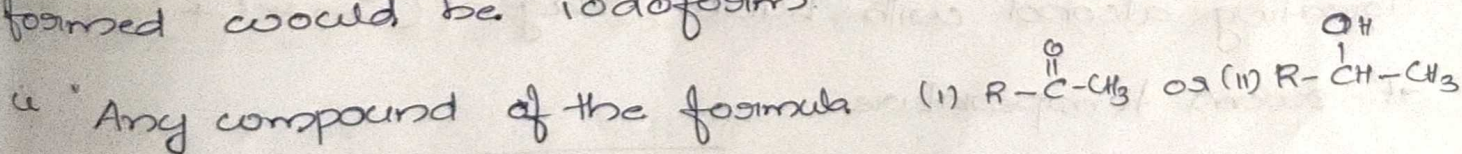


Thus, not only methyl ketones but also (i° or 2°) alcohols.



Iodoform test

If I_2 and alkali is used in haloform rxn, the haloform formed would be iodoform:

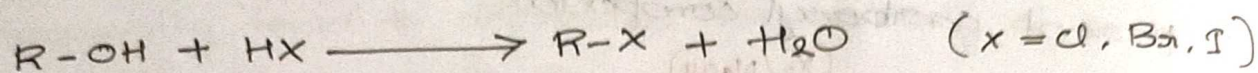


when treated with I_2 & alkali would yield a yellow precipitate of Iodoform.

→ Since it is easily recognizable, this rxn is used as test to detect the presence of $\text{CH}_3\text{-CO-}$ grouping / $\text{CH}_3\text{-CH-OH}$ grouping - Iodoform test

Reaction of alcohols with halogen acids

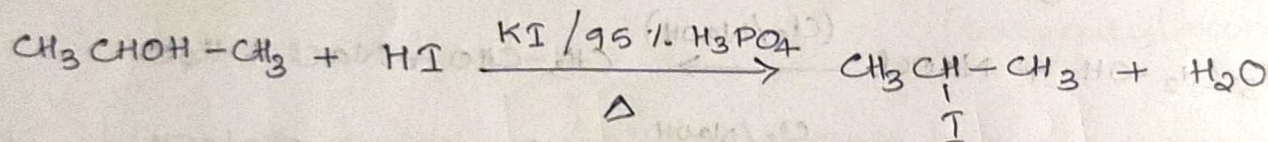
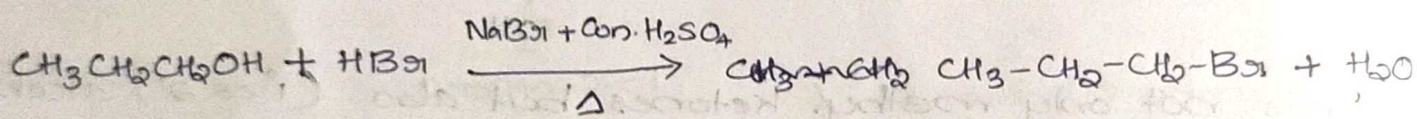
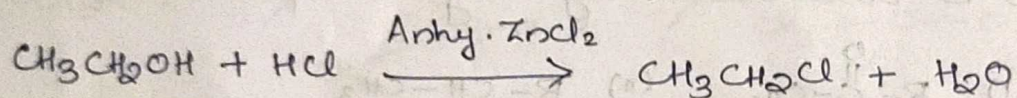
Alcohols are converted into the corresponding alkyl halides by the action of halogen acids; the use of a dehydrating agent like An. $ZnCl_2$ or ~~anhydrous~~ Con. H_2SO_4 being sometimes to facilitate reaction.



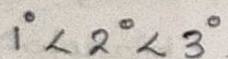
→ Rxn of HCl require the presence of Anhydrous $ZnCl_2$

→ HBr & HI may also be prepared 'in situ' by using

($NaBr + Con. H_2SO_4$) and ($KI + 95\% H_3PO_4$) respectively



→ For a given HX, the reactivity of R-OH is in the order:



Lucas test - Distinction between 1° , 2° and 3° alcohol

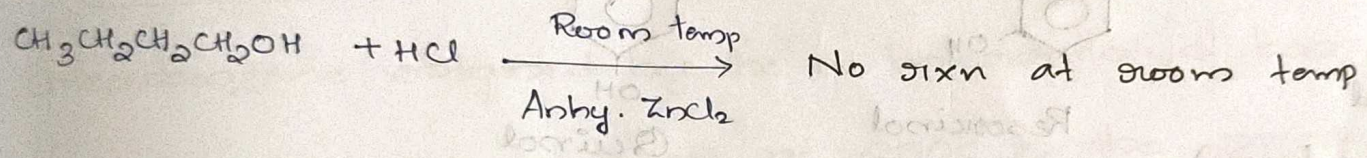
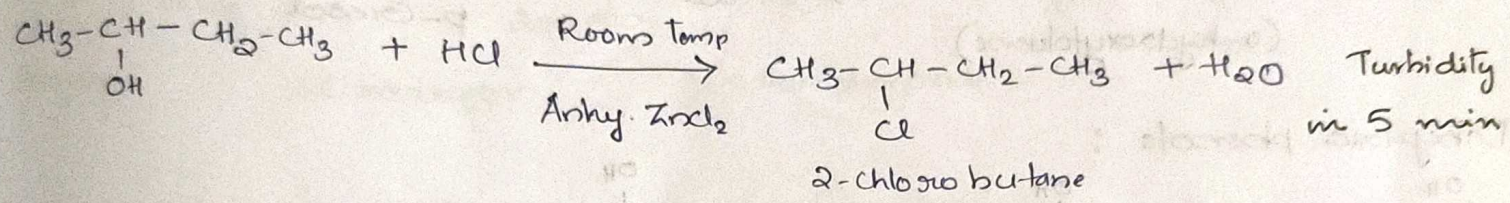
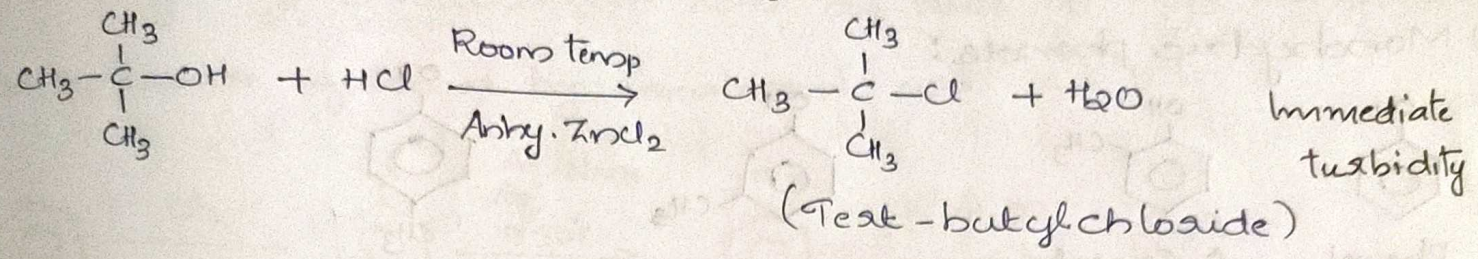
→ Treating alcohol with Lucas reagent (Con. HCl + Anhy. $ZnCl_2$) at room temperature.

→ The order of reactivity ; $1^\circ < 2^\circ < 3^\circ$

→ 3° alcohol →

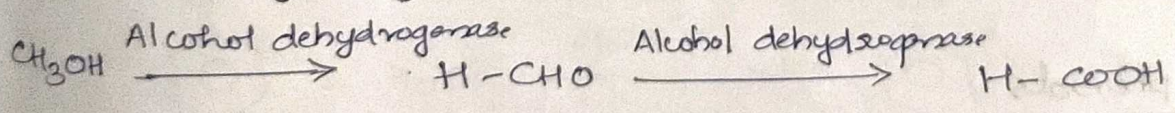
→ Time required for the formation of the insoluble alkyl halide, which is indicated by appearance of turbidity

- (i) 3° alcohol → Immediate turbidity
- (ii) 2° alcohol → Turbidity only in about 5 minutes
- (iii) 1° alcohol → No turbidity (at room temp)



Chemistry of methanol Poisoning

- Methanol is readily absorbed by ingestion as well as inhalation & is toxic to humans.
- cause blindness, metabolic disturbances, leads to coma & death
- Methanol is metabolised into formaldehyde by enzyme alcohol dehydrogenase and then into highly toxic formic acid.

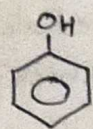


- Formic acid inhibits mitochondrial 'cytochrome c oxidase' causing symptoms of hypoxia, also cause metabolic acidosis.

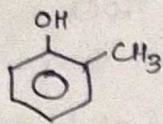
PHENOLS

classification & Nomenclature

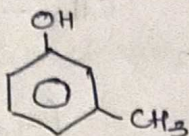
(1) Monohydric phenols:



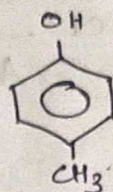
Phenol



o-Cresol
(o-hydroxytoluene)

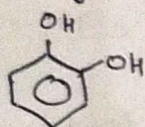


m-Cresol



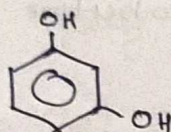
p-Cresol

(2) Dihydric phenols:

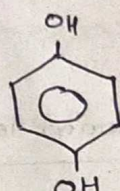


Catechol

(o-dihydroxybenzene)

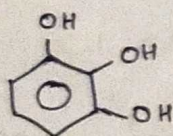


Resorcinol



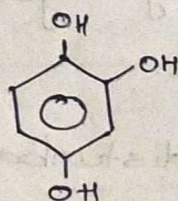
Quinol

(3) Trihydric phenols:



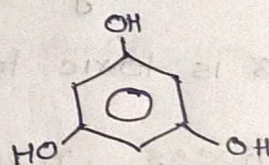
Pyrogallol

(1,2,3-trihydroxybenzene)



Hydroxy Quinol

(1,2,4-trihydroxybenzene)



Phloroglucinol

(1,3,5-trihydroxybenzene)

Source of phenols

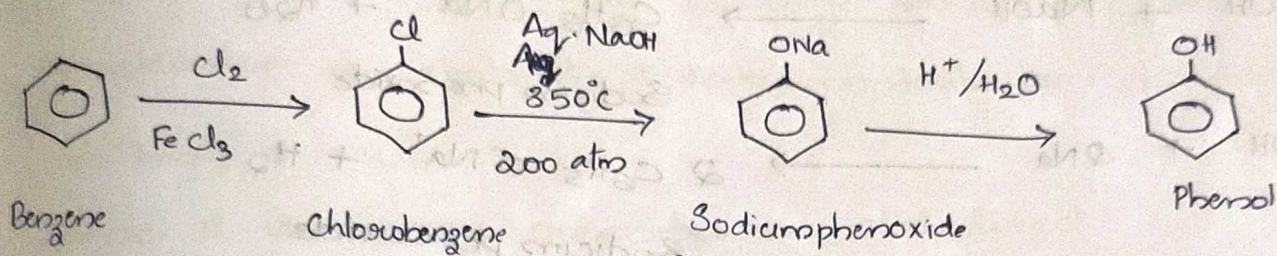
→ Some phenols like phenol, cresol etc are present in coal tar fractions and are obtained industrially from this source.

Eg: phenol is present in the middle oil fraction of coal tar while cresols are present in creosote oil (heavy oil)

Preparation of phenol from chlorobenzene

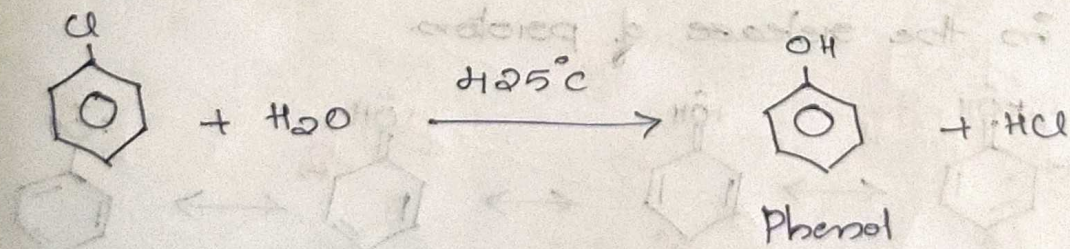
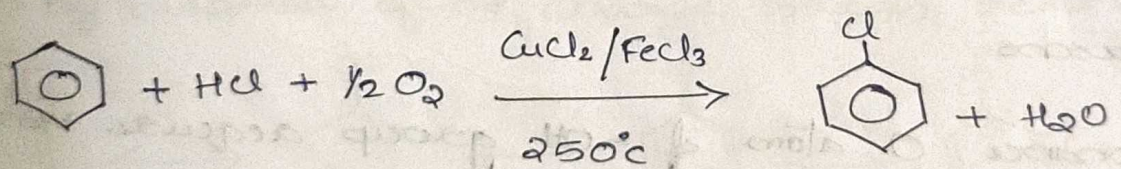
① Dow process

Hydrolysis of chlorobenzene with aq. NaOH at high temperature and pressure followed by treatment with dil. HCl



② Raschig's Process

Chlorobenzene obtained by the interaction of benzene, hydrogen chloride and air at 250°C in the presence of a mixture of cupric chloride and ferric chloride as catalyst, is hydrolysed by superheated steam at 425°C to get phenol & HCl.

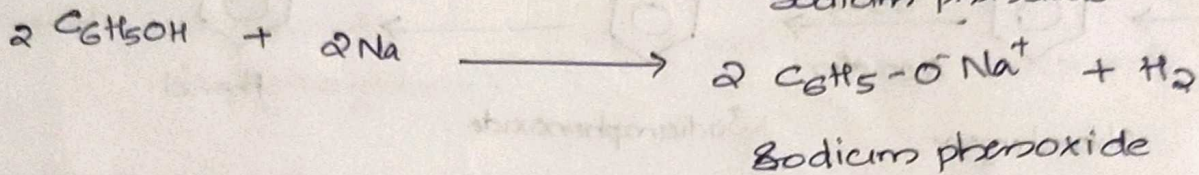
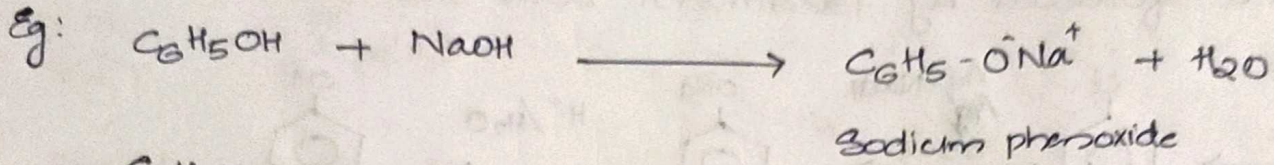
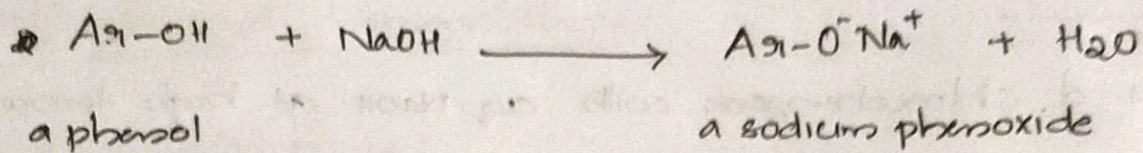
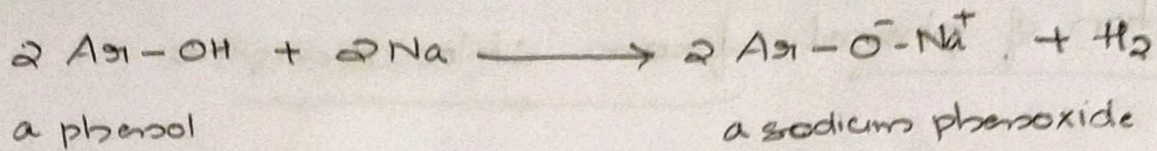


Acidity of phenols

→ Phenols are feebly acidic

→ React with alkali metals & NaOH or KOH to form salts

known as phenoxides.

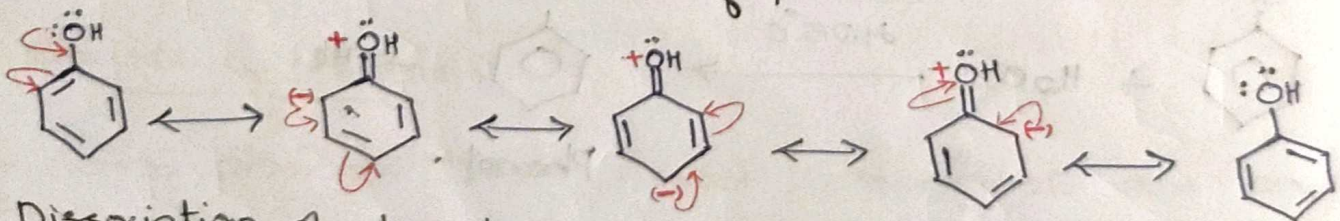


→ Dissociation constant (K_a) of hydroxyl group in phenol is of the order 10^{-10} , carboxylic acid - 10^{-5} and alcohols - between 10^{-16} & 10^{-18}

⇒ phenols are stronger acids than alcohols but weaker acid than carboxylic acid.

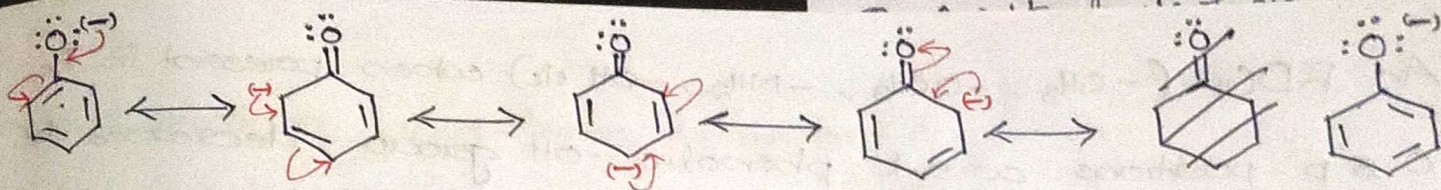
→ The acidic behaviour of phenol may be explained as due to two reasons.

① Due to resonance O atoms of -OH group acquire +ve charge which help in the release of proton.



② Dissociation of phenol to phenoxide ion & a proton, equilibrium lies mainly towards RHS as per the resulting phenoxide ion is more stabilized by resonance as compared to phenol.





→ In phenol, it is dipolar i.e. both +ve & -ve charge
 ⇒ stability is low, contribution to total structure is low

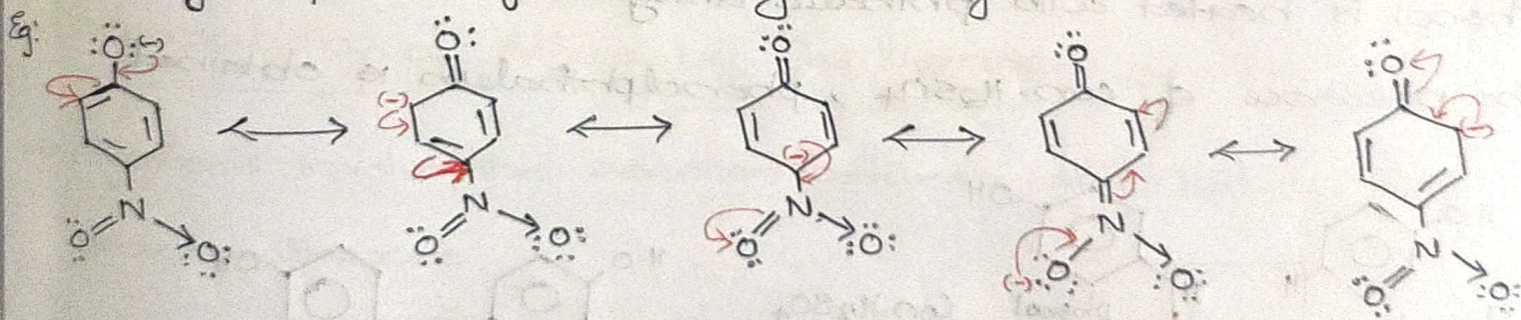
→ In phenoxide, only a -ve charge is spread over the molecules ⇒ stability & total contribution to total structure is high

Hence it is more resonance stabilised

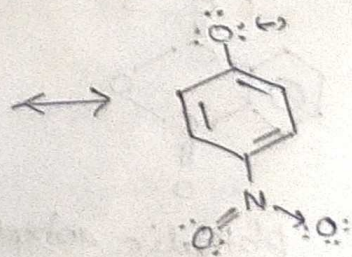
→ This resonance is not possible in alcohol & alkoxide & therefore phenols are more acidic than alcohols

Effect of substituents on acidity of phenol

→ An EWG ($-\text{NO}_2$, $-\text{Cl}$, $-\text{CN}$, $-\text{CHO}$, $-\text{COOH}$ etc) when present in o & p positions w.r.t phenolic group increases the acidity of phenols due to greater stabilisation of phenoxide ion by dispersal of -ve charge through resonance.



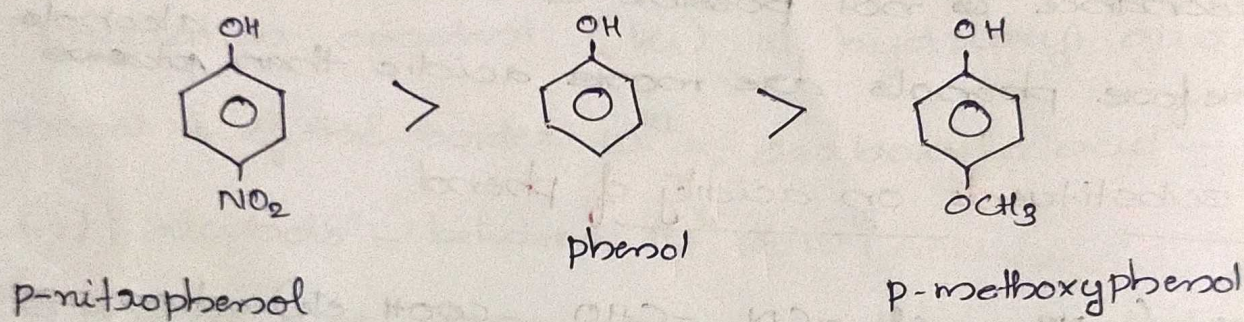
→ Increase acidity (dispersal of -ve charge spread to NO_2 group)



→ p-nitrophenol more acidic than phenol since great tendency to donate a proton

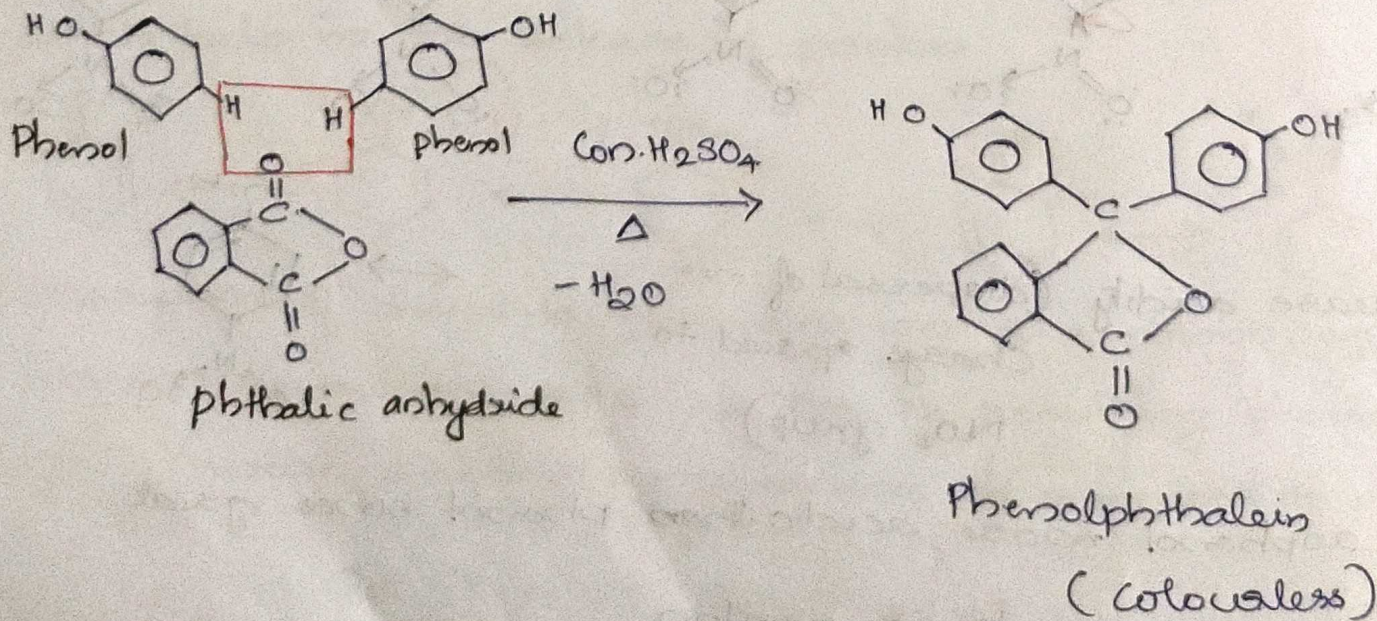
→ An EDG (-CH₃, -OCH₃, -NH₂, -OH etc) when present in the o & p-positions w.r.t phenolic -OH group, decreases the acidity due to destabilisation of phenoxide ion by intensifying the -ve charge through e⁻-releasing +M / +R effect

Eg: p-methoxyphenoxide, OCH₃ grp in para position pumps e⁻ density to ring by +M effect. As a result of increase in charge, destabilise the molecule making it less acidic than phenol.



Phenolphthalein

Phenol is heated with phthalic anhydride in 2:1 ratio in the presence of con. H₂SO₄, phenolphthalein is obtained.



Uses:

- Indicator in acid-base titration.
- Universal indicator
- Its powder is generally applied in small quantity on the currency notes given to corrupt officials demanding bribes as a way to trap them; objects like hand, bag or table-cloths that comes into contact with above marked notes turn pink upon washing with dil. alkali solution
- Used as laxative (now it's not used since carcinogenic)

ETHERS

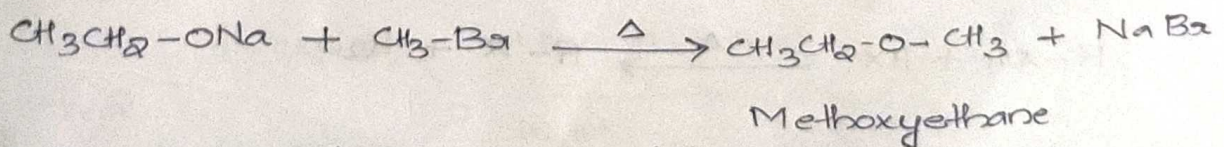
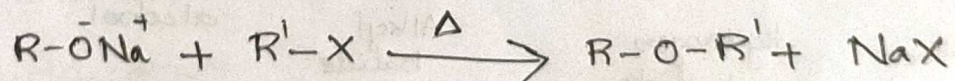
- Compound containing >C-O-C< functional group.
 R-O-R' (R & R' may be same/different)

Table

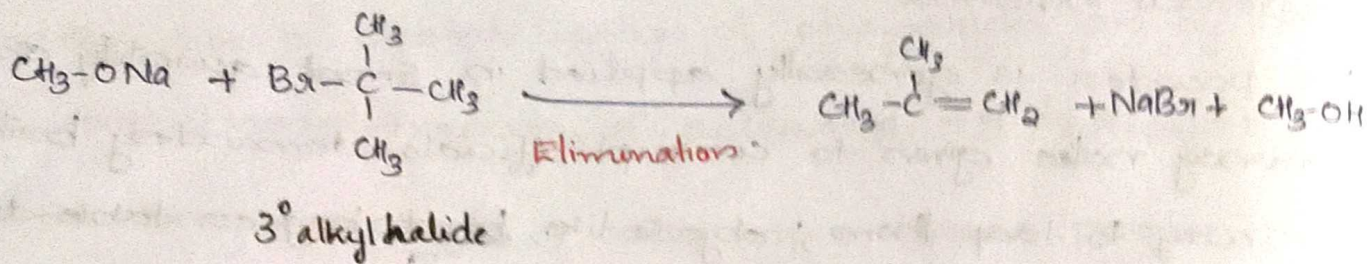
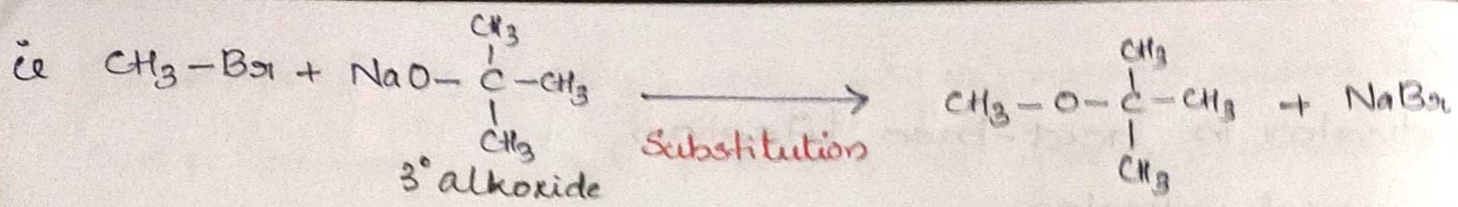
R & R' - Same → Simple / Symmetrical ether
R & R' - diff → Mixed / Unsymmetrical ether

Preparation of ether by 'Williamson Synthesis'

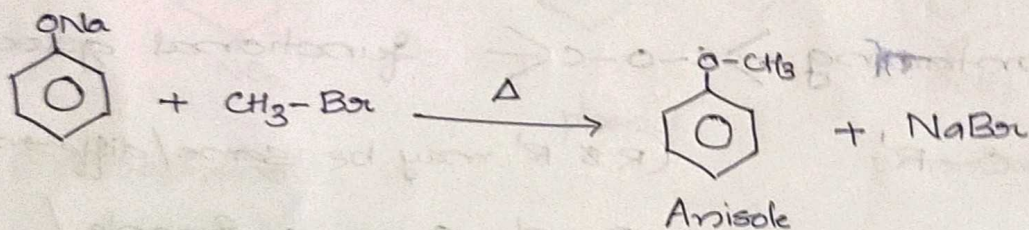
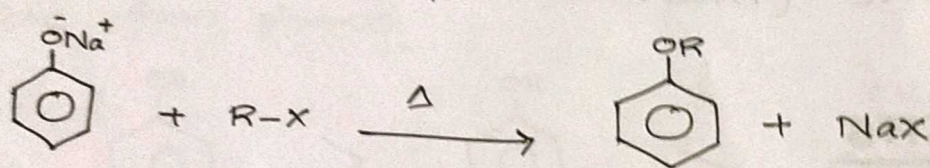
- Synthesis involve the reaction between alkyl halide and sodium alkoxide



- Involve $\text{S}_{\text{N}}2$ reaction, alkoxide (nucleophile)
- Works best with 1° alkyl halide (In 2° & 3° there is a chance of elimination)
- So to make ether containing 2° or 3° alkyl group, that part is taken as alkoxide



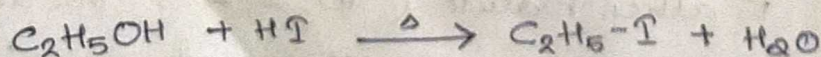
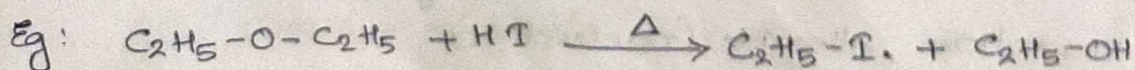
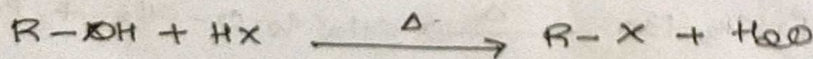
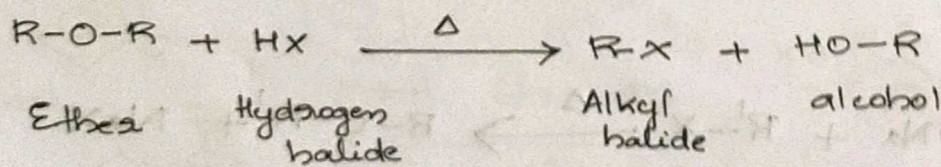
⇒ Alkyl aryl ethers are prepared by the reaction of alkyl halide with sodium phenoxide



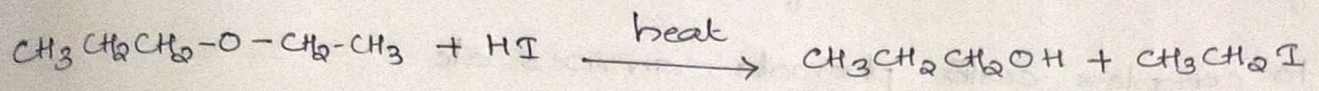
Acidic cleavage of the C-O bond

→ Cleavage of C-O bond in ethers takes place under drastic conditions with excess of hydrogen halides

- Order of reactivity, $\text{HI} > \text{HBr} > \text{HCl}$



→ In mixed ethers, if both alkyl groups are 1° , the halogen goes to smaller alkyl group during cleavage

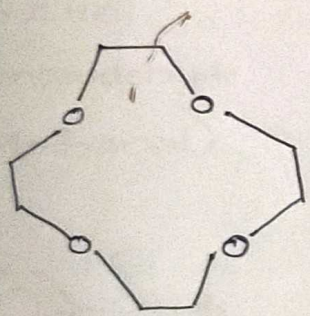


→ Rxn takes place mainly with HBr or HI , because reagents are sufficiently acidic

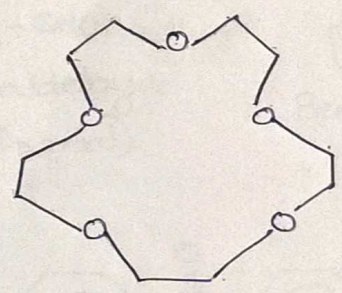
Crown Ethers

→ Macrocyclic polyether

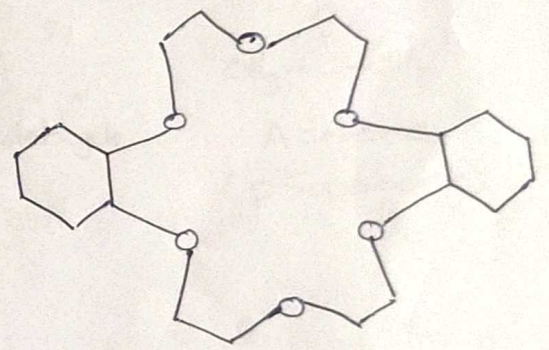
→ it is large ring compounds containing more than 12 C atoms and several ether oxygen atoms.



12-Crown-4



15-Crown-5

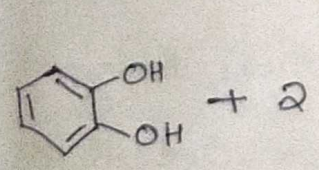


Dicyclohexano-18-Crown-6

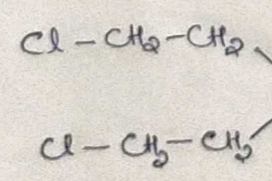
→ 1st numbers indicate - total no. of atoms in ring.

2nd numbers indicate - No. of oxygen atoms.

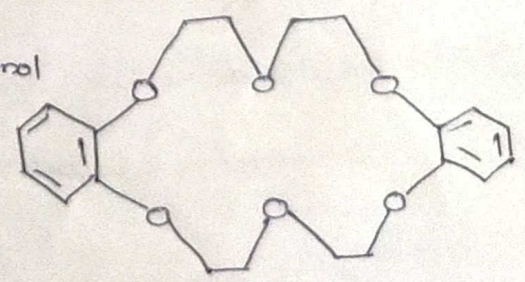
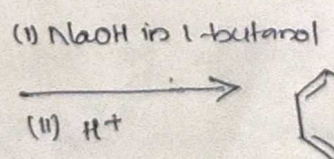
→ Dibenzo-18-crown-6 is prepared by the reaction of catechol with dichlorodiethyl ether in alkaline medium followed by acidification



Catechol



Dichlorodiethyl ether



Dibenzo-18-Crown-6

Properties & applications

dsl

- (1) Used for the resolution of racemic mixtures
- (2) Used to complex with phenols, amines etc
- (3) They have ability of forming complexes with +ve ions such as metallic ions & ammonium ions

Eg: 12-Crown-4 binds Li^+ but not K^+ while

dicyclohexano-18-crown-6 binds K^+ but not Li^+

This method is used for the separation of cations from a mixture.

