ALCOHOL, PHENOL, ETHER

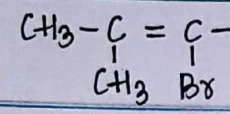
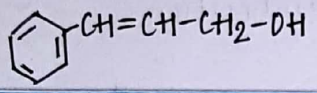
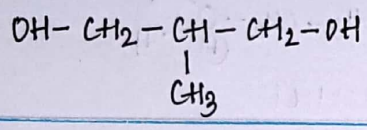
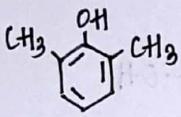
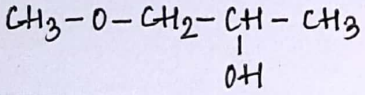
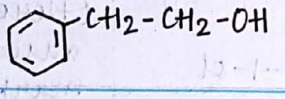
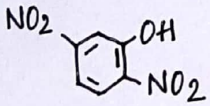
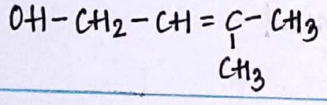
(ORGANIC CHAPTER-2)

ALCOHOL

IUPAC name:- Alkanol

Common name:- Alkyl alcohol

IUPAC names of some alcohols that were asked in board examination:-

STRUCTURAL FORMULA	IUPAC name
1. 	2-bromo-3-methylbut-2-enol
2. 	3-phenylprop-2-en-1-ol
3. 	2-methylpropane-1,3-diol
4. 	2,6-dimethylphenol
5. 	1-methoxypropan-2-ol
6. 	2-phenylethanol
7. 	2,5-dinitrophenol
8. 	3-methylbut-2-en-1-ol

PREPARATION OF ALCOHOLS:-

① FROM ALKENES:-

(i) By acid catalysed hydration:-

$$\text{Alkene} \xrightarrow[H_3O^{\oplus}]{H^{\oplus}} \text{Alcohol}$$

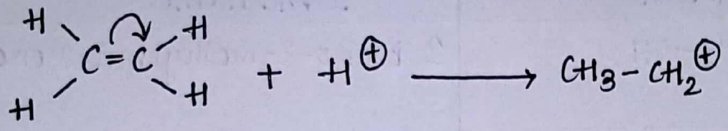
eg:- $CH_2=CH_2 \xrightarrow[H_3O^{\oplus}]{H^{\oplus}} CH_3-CH_2-OH$

$CH_3-CH=CH_2 \xrightarrow[H_3O^{\oplus}]{H^{\oplus}} CH_3-\underset{OH}{CH}-CH_3$

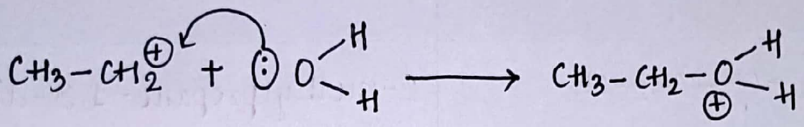
Propene → Propan-2-ol

Mechanism:-

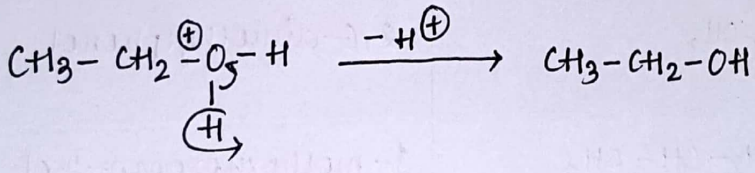
Step-①:- Formation of carbocation



Step-②:- Nucleophilic attack of water on carbocation.



Step-③:- Deprotonation to form an alcohol



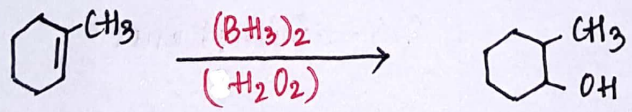
(ii) By hydroboration oxidation:-

$$CH_3-CH=CH_2 \xrightarrow[(H_2O_2)]{(BH_3)_2} CH_3-\underset{OH}{CH}-CH_2-OH$$

Propene → propan-1-ol

(Here, water is added by anti-markovnikov's rule)

Eg:-

(a) 

In this process, primary alcohol is formed.

(b) $CH_3-\underset{CH_3}{\overset{CH_3}{C}}=CH_2 \xrightarrow[(H_2O_2)]{(BH_3)_2} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-OH$

(2) FROM CARBONYL COMPOUND:-

(i) $H-\underset{\underset{O}{\|}}{C}-H + \overset{\ominus}{CH_3}-\overset{\oplus}{MgBr} \longrightarrow H-\underset{CH_3}{\overset{O-MgBr}{\overset{|}{\underset{|}{C}}}}-H \longrightarrow CH_3CH_2OH$

Eg:-

$CH_3-\underset{\underset{O}{\|}}{C}-H + \overset{\ominus}{CH_3}-\overset{\oplus}{MgBr} \longrightarrow CH_3-\underset{CH_3}{\overset{O-MgBr}{\overset{|}{\underset{|}{C}}}}-H \longrightarrow CH_3-\underset{CH_3}{\overset{OH}{\overset{|}{\underset{|}{C}}}}-H$

(ii) Reduction of aldehydes and ketones:-

In Aldehyde,

$$R-CHO \xrightarrow[H_3O^{\oplus}]{LiAlH_4} R-CH_2OH \ (1^{\circ}\text{Alcohol})$$

Eg:- $CH_3-\underset{\underset{O}{\|}}{C}-H \xrightarrow[H_3O^{\oplus}]{LiAlH_4} CH_3-\overset{OH}{\overset{|}{C}}H-H$

Ethanal → Ethanol (1° Alcohol)

In Ketone,

$$R-\underset{\underset{O}{\|}}{C}-R' \xrightarrow[H_3O^{\oplus}]{LiAlH_4} R-\overset{OH}{\overset{|}{C}}H-R'$$

(2° Alcohol)

Eg:- $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[H_3O^{\oplus}]{LiAlH_4} CH_3-\underset{OH}{\overset{|}{C}}H-CH_3$

Propanone → Propan-2-ol

(iii) Reduction of carboxylic Acid and ester:-

In carboxylic acid,

$$R-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[H_3O^{\oplus}]{LiAlH_4} R-CH_2-OH$$

(1° Alcohol)

Eg:- $CH_3-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[H_3O^{\oplus}]{LiAlH_4} CH_3-CH_2-OH$

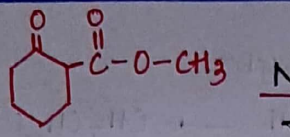
Acetic acid → Ethanol

In ester,

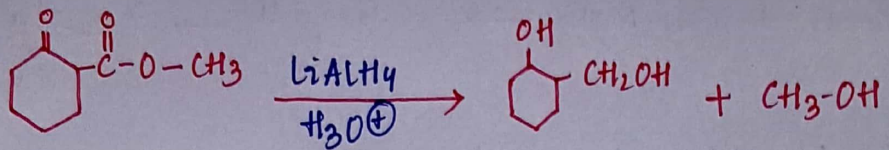
$$R-COOR' \xrightarrow[\text{or } Na/C_2H_5OH]{LiAlH_4} R-CH_2OH + R'OH$$

(1° Alcohol)

Eg:- (i) $CH_3-COOC_2H_5 \xrightarrow[H_3O^{\oplus}]{LiAlH_4} CH_3-CH_2-OH + C_2H_5OH$

(ii)  $\xrightarrow[H_3O^{\oplus}]{NaBH_4}$ Can't Reduce

* $NaBH_4$ cannot reduce ester whereas $LiAlH_4$ can.



③ FROM GRIGNARD REAGENTS:-

(i) $CH_3MgBr + HCHO \xrightarrow{H^{\oplus}}$ 1° Alcohol

Eg:-

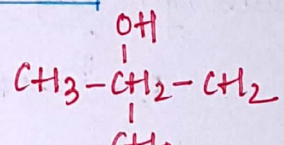
$CH_3MgBr + HCHO \xrightarrow{H^{\oplus}} CH_3CH_2OH$

$CH_3CH_2MgBr + HCHO \xrightarrow{H^{\oplus}} CH_3CH_2CH_2OH$

(ii) CH_3MgBr + Any other aldehyde $\xrightarrow{H^{\oplus}}$ 2° Alcohol

Eg:- $CH_3MgBr + CH_3CH_2CHO \xrightarrow{H^{\oplus}} CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$

(iii) CH_3MgBr + Ketone $\xrightarrow{H^{\oplus}}$ 3° Alcohol

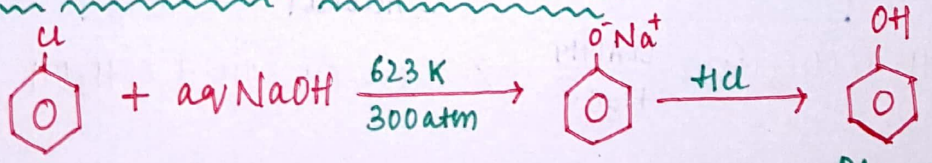
Eg:- $CH_3MgBr + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{H^{\oplus}}$ 

Acetone

2-Methylpropan-2-ol

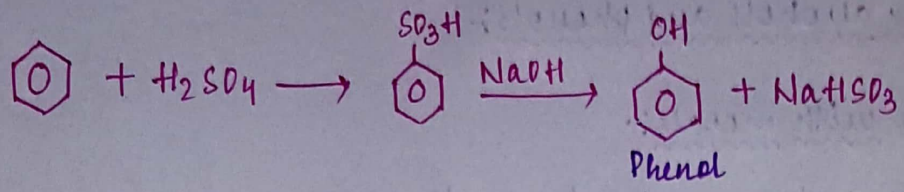
PREPARATION OF PHENOL:-

① From haloarenes / chlorobenzene:-

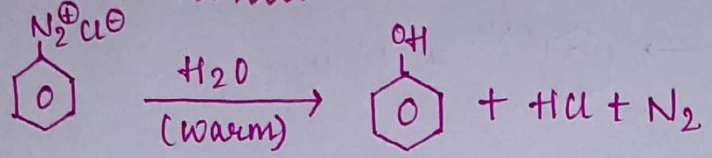


Phenol

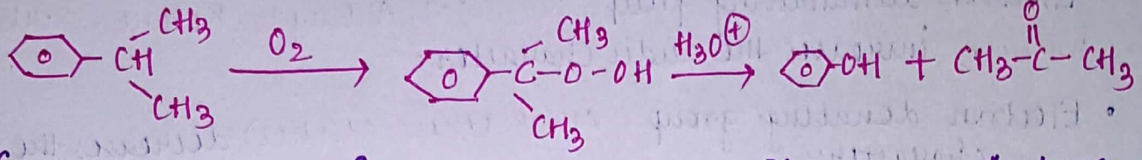
② From benzene sulphonic acid :-



③ From diazonium salt :-



④ From Cumene :-



Cumene — Cumenehydroperoxide — Phenol — Acetone

PHYSICAL PROPERTIES :-

(i) BOILING POINT :- More the number of C-atoms in the straight chain, more surface area, more vanderwall force so more boiling point. The boiling point decreases with branching

(ii) SOLUBILITY :- Alcohols are soluble in water due to intermolecular hydrogen bonding. Lower alcohols are soluble in water. On increasing the number of carbon chain, due to +I effect of alkyl group, the polarity of OH decreases, so the tendency to form hydrogen bond decreases. So higher alcohols are less soluble or insoluble in water.

CHEMICAL PROPERTIES :-

Alcohols have two types of bond breaking reaction.

(a) C-O bond breaking (b) O-H bond breaking

* C-O bond of alcohol will break when it undergoes nucleophilic substitution reaction. So the bond between C-O is broken when they react as electrophiles.

* The bond between O-H is broken when alcohols react as nucleophiles.

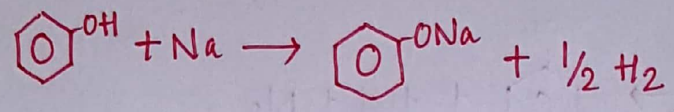
(a) Reactions involving cleavage of O-H bond:-

1. Acidity of alcohols and phenols:-

(i) Reaction with metals:-

$$R\text{-}OH + Na \longrightarrow RONa + \tfrac{1}{2} H_2$$

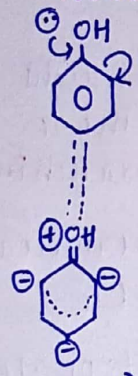
Eg:-



(ii) Acidic nature of alcohol:-

- Electron withdrawing group (NO_2, CN, Aldehyde, Ketone, carboxylic acid, halogen) increases the acidic character.
- Electron donating group (Alkyl, ether, alcohol) decreases the acidic character

(iii) Acidity of phenols:-



(Phenol)

In case of phenol, due to resonance charge separation is there. So kinetically, its energy is increased which leads to lesser stability.



(Phenoxide ion)

In case of phenoxide ion, only negative charge is delocalised, so there is no charge separation. So, phenoxide ion is more stable.

(b) Reactions involving cleavage of carbon-oxygen bond in alcohols:-

① Dehydration of alcohol:-

Here, conc H_2SO_4 or conc H_3PO_4 act as dehydrating agent.

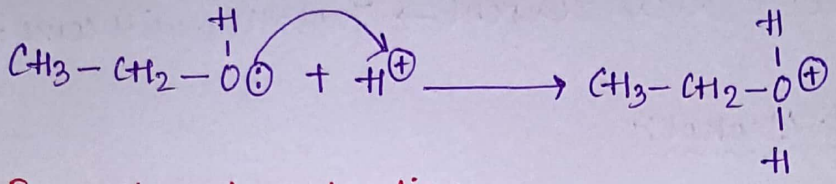
$$\text{Alcohol} \xrightarrow[443\,K]{\text{conc } H_2SO_4} \text{Alkene}$$

$$CH_3-CH_2-OH \xrightarrow[443\,K]{\text{conc } H_2SO_4} CH_2=CH_2$$

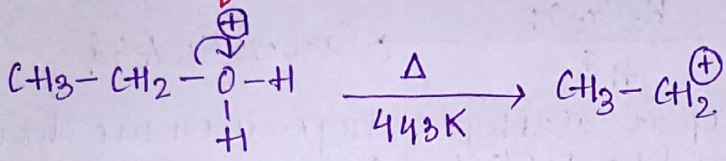
Ethanol → Ethene

Mechanism:-

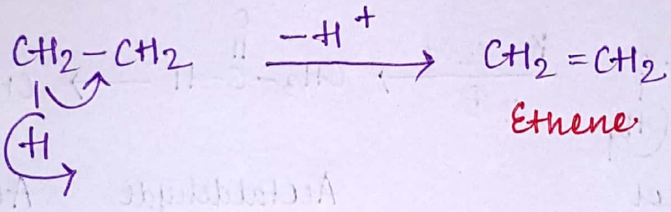
① Formation of protonated alcohol



② Formation of carbocation



③ Deprotonation



Ethene

Secondary and Tertiary alcohols are dehydrated under milder conditions. For example:-

$$CH_3-\underset{OH}{CH}-CH_3 \xrightarrow[440\,K]{85\%\ H_3PO_4} CH_3-CH=CH_2 + H_2O$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[358\,K]{20\%\ H_3PO_4} CH_3-\overset{CH_2}{\underset{\|}{C}}-CH_3 + H_2O$$

The relative ease of dehydration of alcohols follows the following order:- Tertiary > Secondary > Primary.

② Reaction with hydrogen halides :-

(Lucas test)

The difference in reactivity of three classes of alcohols with Lucas reagent (Conc HCl + Anhy. $ZnCl_2$) distinguishes them from one another.

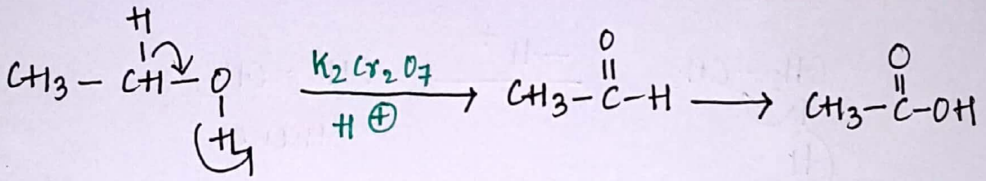
1° Alcohol + Lucas reagent	→ Turbidity will not come at room temp.
2° Alcohol + Lucas reagent	→ Turbidity will come after 2-3 min.
3° Alcohol + Lucas reagent	→ Turbidity will come suddenly

③ Oxidation of Alcohol :-

1° Alcohol $\xrightarrow[H^{\oplus}]{K_2Cr_2O_7}$ Carboxylic Acid

★ If we want to stop at aldehyde stage, then we should use reagents like PCC/CrO_3 / Cu powder at 573 K.

Eg :-

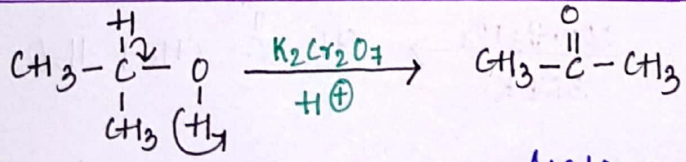


$CH_3-CH_2-OH \xrightarrow{PCC} CH_3-CHO$

Ethyl alcohol — Acetaldehyde

2° Alcohol $\xrightarrow[H^{\oplus}]{K_2Cr_2O_7}$ Ketone

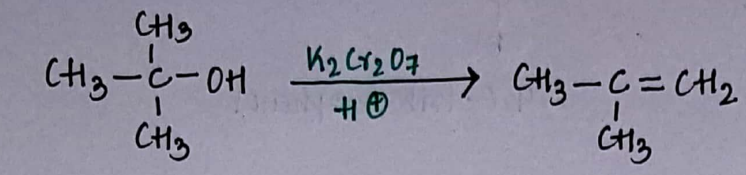
Eg :-



Isopropyl alcohol — Acetone

3° Alcohol $\xrightarrow[H^{\oplus}]{K_2Cr_2O_7}$ Alkene

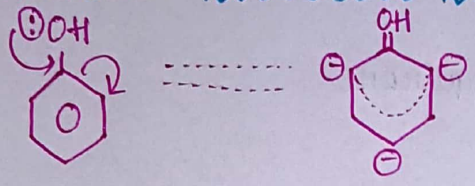
Eg:-



2-Methylpropan-2-ol 2-Methylpropene

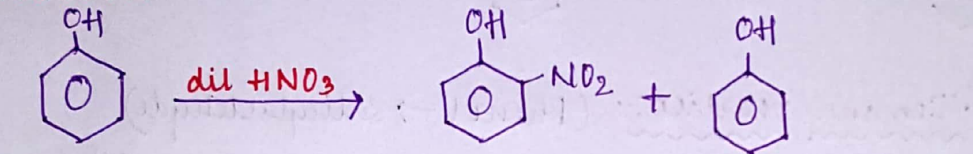
(c) Reaction of phenols:-

1. Electrophilic substitution reaction:-



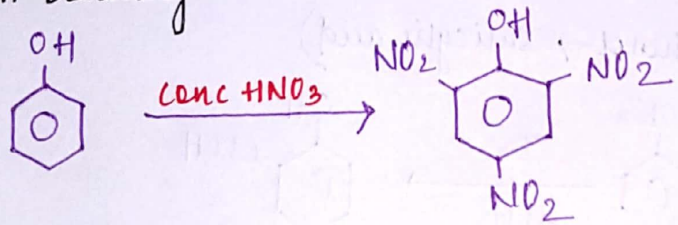
As, negative charge is delocalised at ortho and para position. So it is a ring activating group.

(i) Nitration:-



Phenol o-Nitrophenol p-Nitrophenol

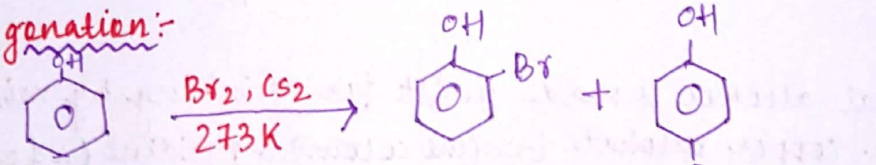
The ortho and para isomers can be separated by steam distillation. o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-Nitrophenol is less volatile due to intermolecular hydrogen bonding.



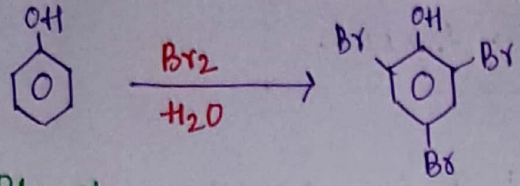
Phenol 2,4,6-Trinitrophenol (Picric acid)

(ii) Halogenation:-

(a)

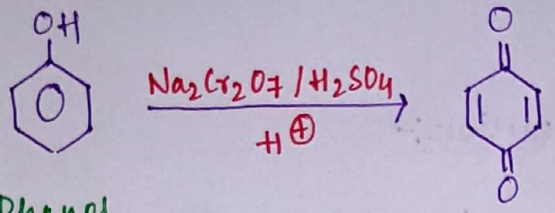


Phenol Minor Major

(b) 

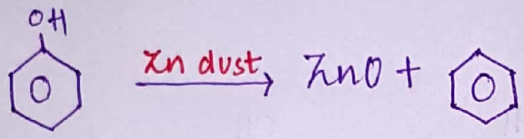
Phenol — 2,4,6-Tribromophenol

(2) Oxidation of phenol:-

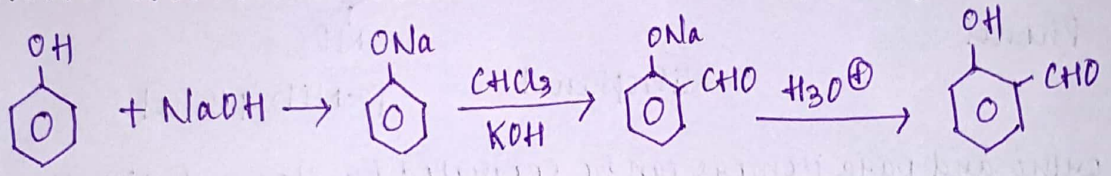


Phenol — Benzoquinone

(3) Reaction with zinc dust:-

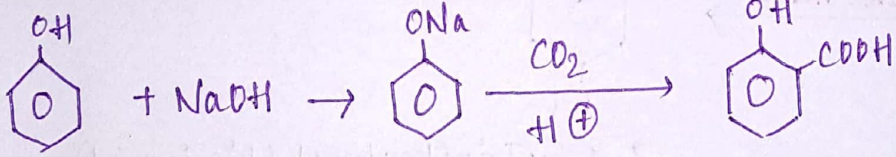


(4) Reimer-Tiemann reaction:- (Phenol → salicylaldehyde)



Phenol — Salicylaldehyde

(5) Kolbe's reaction:- (Phenol → salicylic acid)



Phenol — Salicylic acid

The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give colour) & pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

PREPARATION OF ETHERS :-

① Dehydration of alcohol :-

At 413 K, two OH groups elimination of water takes place.

(a) CH_3CH_2OH, CH_3CH_2OH $\xrightarrow[413\,K]{conc\ H_2SO_4}$ $CH_3CH_2-O-CH_2-CH_3$

Ethanol — Ethoxyethane

MECHANISM :-

Step-① :- Protonation.

$CH_3-CH_2-\ddot{O}H + H^{\oplus} \longrightarrow CH_3-CH_2-\overset{\oplus}{O}H$

Step-② :- Formation of carbocation.

$CH_3-CH_2-\overset{\oplus}{O}H \longrightarrow CH_3-CH_2-\overset{\oplus}{O}(H)-CH_2-CH_3$

$CH_3-CH_2-\ddot{O}-H$

Step-③ :- Deprotonation

$CH_3-CH_2-\overset{\oplus}{O}(H)-CH_2-CH_3 \longrightarrow CH_3-CH_2-O-CH_2-CH_3$

(b) CH_3CH_2OH $\xrightarrow[443\,K]{conc\ H_2SO_4}$ $CH_2=CH_2$

Ethanol — Ethene

② WILLIAMSON SYNTHESIS :-

$R-O-Na + XR' \longrightarrow ROR'$

Alkyl Halide

Eg :-

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-Na + Br-CH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3$

Better results are obtained if alkyl halide is primary. In case of 2° or 3° alkyl halide, elimination predominates over substitution. In case of 3° alkyl halide, alkene is formed instead of ether

PHYSICAL PROPERTIES:-

Boiling Point :- Carboxylic acid > Alcohol > Aldehyde > Ketone > Ether > Alkane

CHEMICAL PROPERTIES:-

Case-I :- If alkyl group is 1° or 2°

Eg:- ① $CH_3-O-CH_2-CH_3 + HI \rightarrow CH_3I + CH_3CH_2OH$ (Iodine is attached to Less hindered side)

② $CH_3-CH_2-O-\underset{CH_3}{\overset{CH_3}{CH}} + HI \rightarrow CH_3CH_2I + \underset{CH_3}{\overset{CH_3}{CH}}-OH$

Case-II :- If alkyl group is 3°

Eg:- $CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + HI \rightarrow \underset{CH_3}{\overset{CH_3}{CI}}-CH_3 + CH_3CH_2OH$ (Iodine will attach to the side which is 3°)

Case-III :- If one side of alkyl group is phenyl

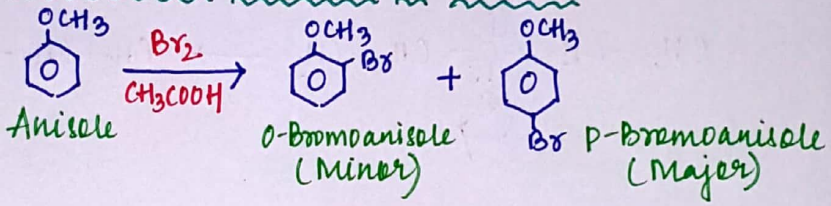
Eg:- $C_6H_5-O-CH(CH_3)_2 + HI \rightarrow C_6H_5OH + \underset{CH_3}{\overset{CH_3}{CH}}-I$ (The phenyl group become phenol i.e C_6H_5OH)

Case-IV :- If one side is benzyl or allyl

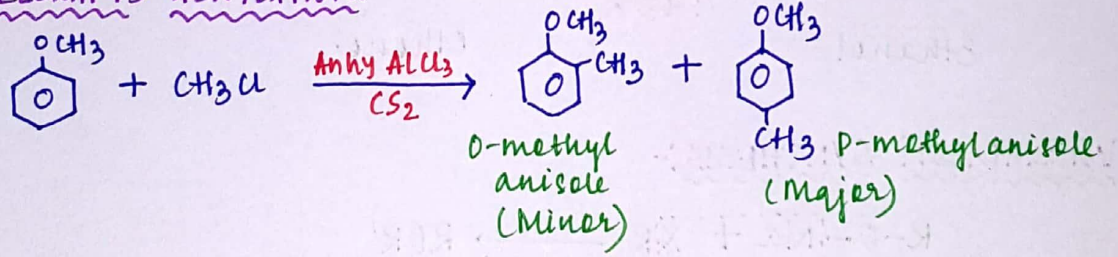
Eg:- $C_6H_5-CH_2-O-CH_2-CH_3 + HI \rightarrow C_6H_5-CH_2I + CH_3-CH_2-OH$ (The benzyl group becomes $C_6H_5-CH_2I$)

② ELECTROPHILIC SUBSTITUTION REACTION OF ANISOLE:-

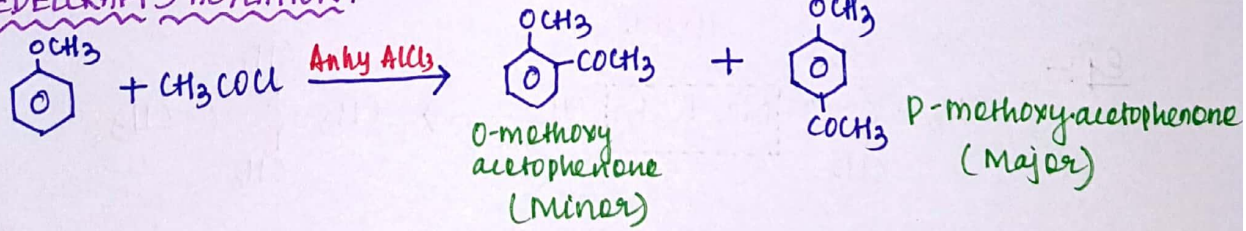
① Halogenation:-



② FRIEDELCRAFT'S ALKYLATION:-



③ FRIEDELCRAFT'S ACYLATION:-



④ NITRATION:-

