Alcohol, Phenol & Ether

ETHER

ether

* Common & IUPAC name for Ethers:

1.) CH_3OCH_3 CN: Dimethyl ether
IUPAC: Methoxymethane

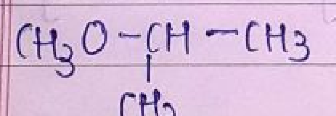
2.) $C_2H_5OC_2H_5$ CN: Diethyl ether
IUPAC: Ethoxyethane.

3.) $CH_3OCH_2CH_2CH_3$ CN: Methyl-n-propyl ether
IUPAC: 1-Methoxypropane

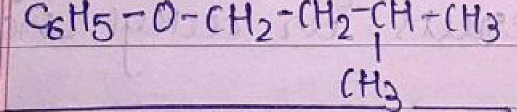
4.) $C_6H_5OCH_3$ CN: Methyl phenyl ether (Anisole)
IUPAC: Methoxybenzene (Anisole)

5.) $C_6H_5OCH_2CH_3$ CN: Ethyl phenyl ether (Phenetole)
IUPAC: Ethoxybenzene

6.) $C_6H_5O(CH_2)_6-CH_3$ CN: Heptyl phenyl ether
IUPAC: 1-Phenoxyheptane

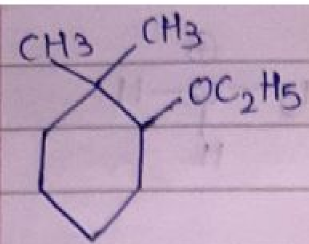
7.) 

$CH_3O-\underset{CH_3}{CH}-CH_3$ CN: Methyl isopropyl ether
IUPAC: 2-Methoxypropane

8.) 

$C_6H_5-O-CH_2-CH_2-\underset{CH_3}{CH}-CH_3$ CN: Phenyl isopentyl ether
IUPAC: 3-Methylbutoxybenzene

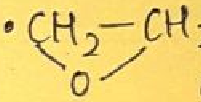
9.) $CH_3-O-CH_2-CH_2-OCH_3$ IUPAC: 1,2-Dimethoxyethane

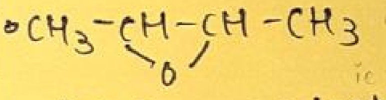
10.) 

IUPAC: 2-Ethoxy-1,1-dimethyl cyclohexane.

* R—O—R Simple ether
* R—O—R' Mixed ether

Cyclic Ether (epoxy)

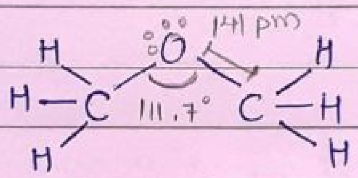
- 
CH_2-CH_2 (O) Epoxy ethane (ethylene oxide)

- 
$CH_3-CH-CH-CH_3$ (O)

इसका cleavag हमेशा Term पे ही होगा। ie: $CH_3-\overset{\oplus}{CH}-CH_2$ $O^{\ominus}$

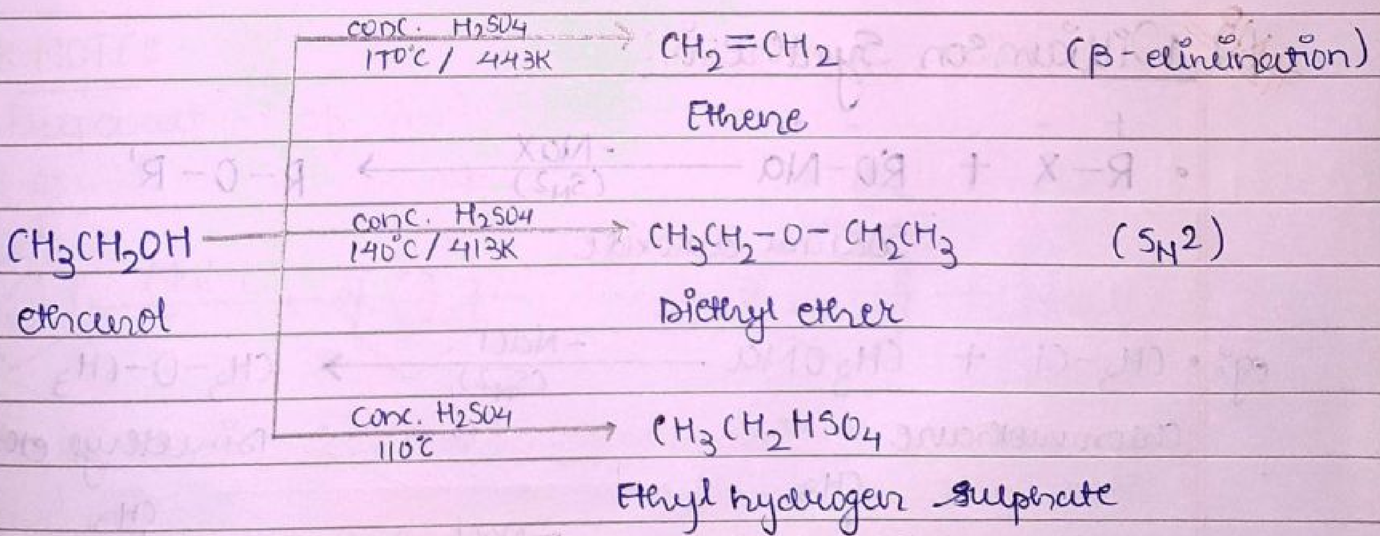
→ 2,3 epoxy butane

* Structure of ether:



* Preparation:

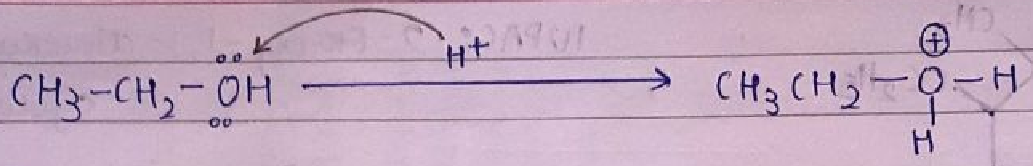
A.) By dehydration of Alcohol:



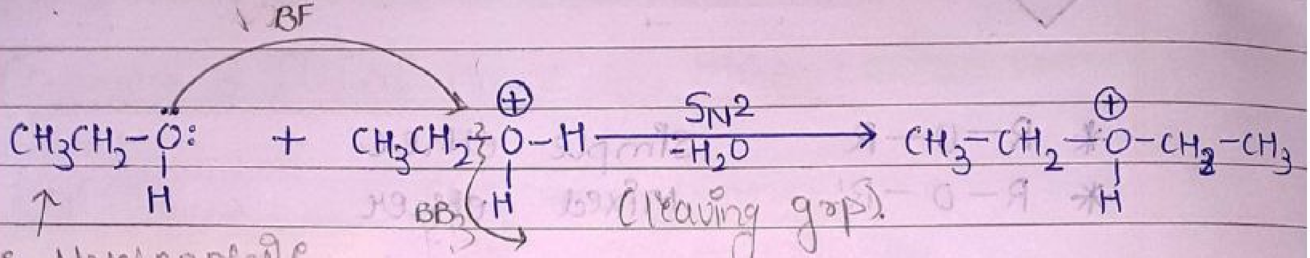
★ Mechanism:

- Formation of ether is a nucleophilic bimolecular rxn (S_N2) involving alcohol molecules attack over a protonated alcohol as shown:

1.)


$$CH_3-CH_2-\ddot{O}H \xrightarrow{H^+} CH_3CH_2-\underset{H}{\overset{\oplus}{O}}-H$$

2.)

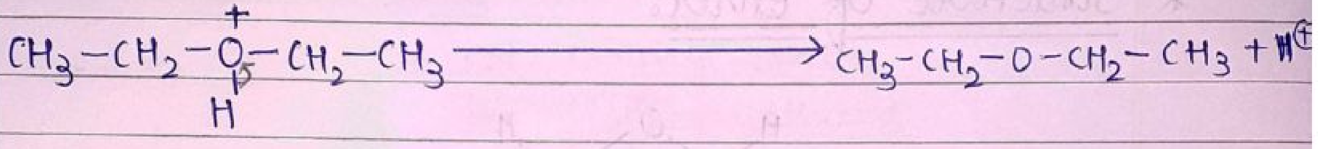


$$CH_3CH_2-\underset{H}{\ddot{O}}: + CH_3CH_2-\underset{H}{\overset{\oplus}{O}}-H \xrightarrow[-H_2O]{S_N2} CH_3-CH_2-\underset{H}{\overset{\oplus}{O}}-CH_2-CH_3$$

(leaving grp)

acts as Nucleophile

3.)


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

*** NOTE:**
- NO carbocation formed.
- Transition state is an intermediate.

B.) From Alkyl Halide:

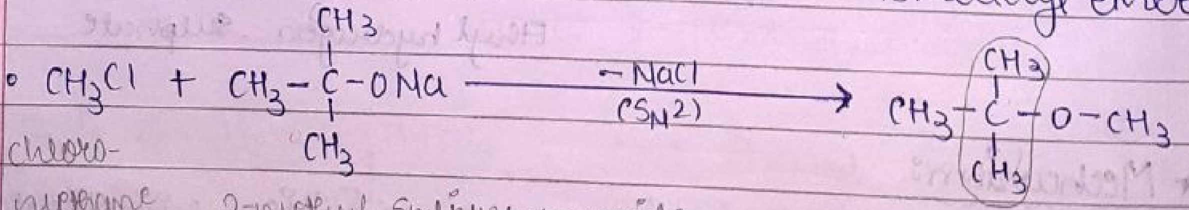
NB 1.) Williamson Synthesis:

• $\overset{+}{R}-\overset{-}{X} + R'\overset{-}{O}-\overset{+}{Na} \xrightarrow[(S_N2)]{-NaX} R-O-R'$

Sodium alkoxide

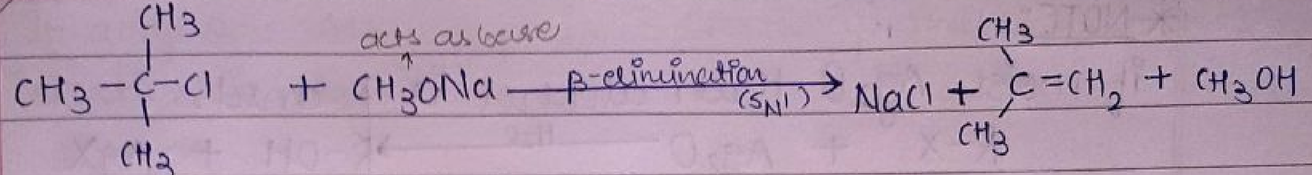
eg: • $CH_3-Cl + CH_3ONa \xrightarrow[(S_N2)]{-NaCl} CH_3-O-CH_3$

Chloromethane   Sodium methoxide   Dimethyl ether


$$\bullet\ CH_3Cl + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-ONa \xrightarrow[(S_N2)]{-NaCl} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3$$

chloromethane   2-methyl Sodium propoxide   2 methoxy (2 methyl) propane imp

an actual, not Williamson



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl + \overset{\text{acts as base}}{CH_3ONa} \xrightarrow[(S_N1)]{\beta\text{-elimination}} NaCl + \overset{CH_3}{\underset{CH_3}{>}}C=CH_2 + CH_3OH$$

Chloro Isobutane　Sod. methoxide　Isobutene　methanol

*** NOTE:**

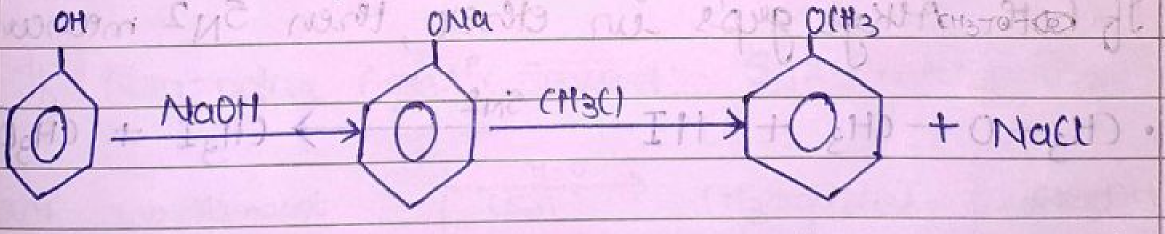
- Because of alkoxides not being only nucleophile but strong base as well.
- They react with alkyl halides leading to elimination reaction.

*** NOTE:**

- Williamson synthesis is the best method to produce any kind of ether (simple / mixed).
- Only primary halides gives the following rxn.
- S_N2 mechanism is carried out.
- No carbocation formation.

*** NOTE:**

- Preparation of Anisole:



Phenol　Sod. Phenoxide　Anisole　Sod. Chloride

2.) From Silver Oxide:

- $2R-X + \text{Dry } Ag_2O \longrightarrow R-O-R + 2AgX.$

*** NOTE:**

- if moist Ag_2O then alcohol is formed.

$$R{-}X + Ag_2O \xrightarrow{H_2O} R{-}OH + AgX$$

* Physical Properties:

1.) Boiling Point:

- BP of alcohol is greater than ether as ethanol have a strong intermolecular hydrogen bond.

2.) Solubility:

- Initially ethers are water soluble due to formation of intermolecular hydrogen bond.
- Higher ethers are soluble in organic solvent.

* Chemical Properties:

A.) Rxn with Normal / Cold HI: (limited quantity)

CASE:1 If both Alkyl grp's are in ether, then S_N2 mechanism occur:

- $\overset{\oplus}{CH_3} \wr \overset{\ominus}{O} - CH_3 + \overset{\oplus}{H}\overset{\ominus}{I} \xrightarrow{S_N2} CH_3I + CH_3OH.$

Methoxy methane — Iodomethane — Methanol

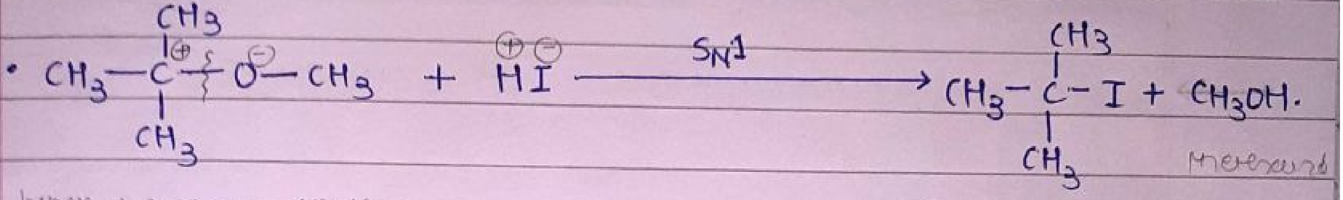
- $\overset{\oplus}{CH_3} \wr \overset{\ominus}{O} - CH_2 - CH_3 + HI \xrightarrow{S_N2} CH_3I + CH_3CH_2OH$

agr ek 1° & dujra 2°/3° then nature ~~of~~ solvent decides the mechanism will be S_N1/S_N2.

Mechanism:

$$CH_3-\ddot{O}-CH_2CH_3 \xrightarrow[HI]{H^{\oplus}} CH_3 \overset{BB}{-} \underbrace{\overset{\oplus}{O}(H)}_{\text{leaving grp}} -CH_2CH_3 \xrightarrow{I^{\ominus}\ \text{nucleophile}} CH_3I + CH_3CH_2OH$$

CASE:2 If any one Alkyl grp is 3° (tertiary) then mechanism of the reaction is S_N1.



$$\cdot\ CH_3-\overset{CH_3}{\underset{CH_3}{\overset{\oplus}{C}}}-\overset{\ominus}{O}-CH_3 + \overset{\oplus\ominus}{HI} \xrightarrow{S_N1} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-I + CH_3OH.$$

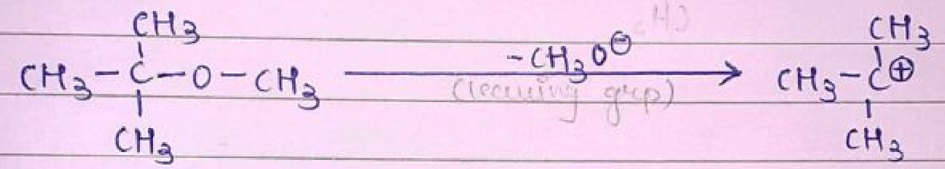
1-methyl-2-propoxy methane

1-Iodo-1-methyl Propane

Methanol

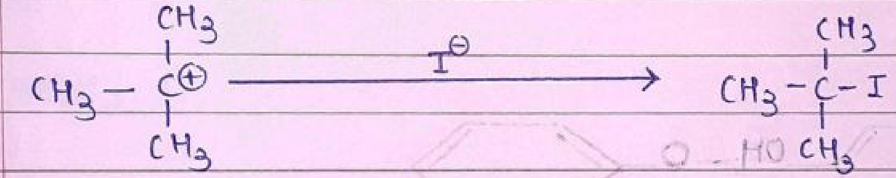
Mechanism:

STEP:1



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_3 \xrightarrow[\text{(leaving grp)}]{-CH_3O^{\ominus}} CH_3-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}}$$

STEP:2

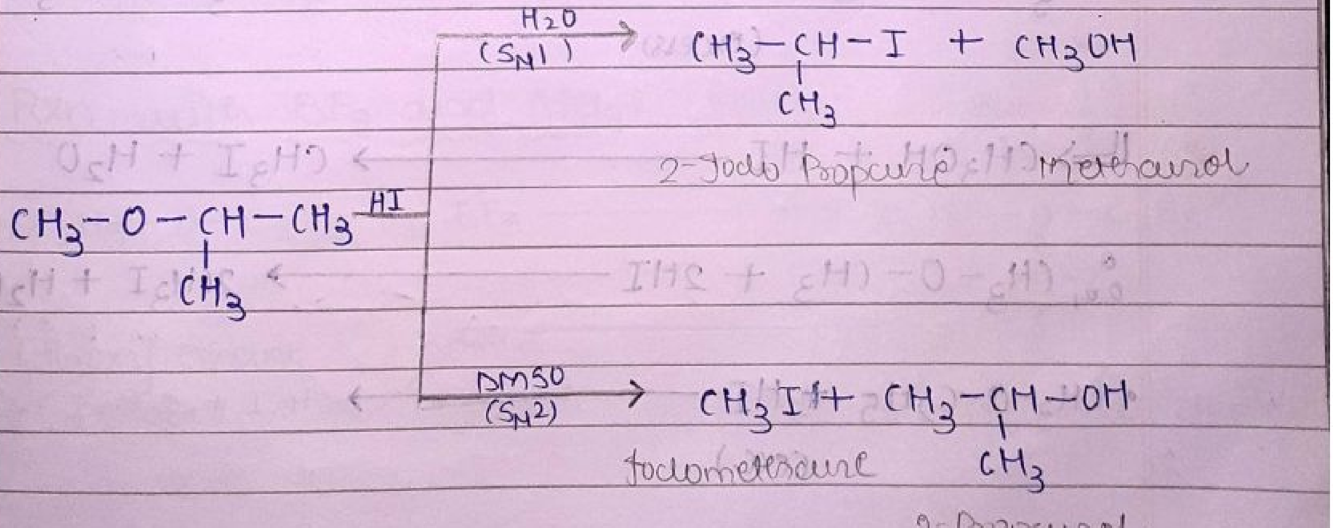


$$CH_3-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} \xrightarrow{I^{\ominus}} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-I$$

CASE:3 If any Alkyl grp is a 2° (secondary) then mechanism of the reaction depends upon the nature of solvent

- If Polar Protic Solvent ; S_N1 mechanism.
- If Non-polar Aprotic Solvent; S_N2 mechanism.

eg:



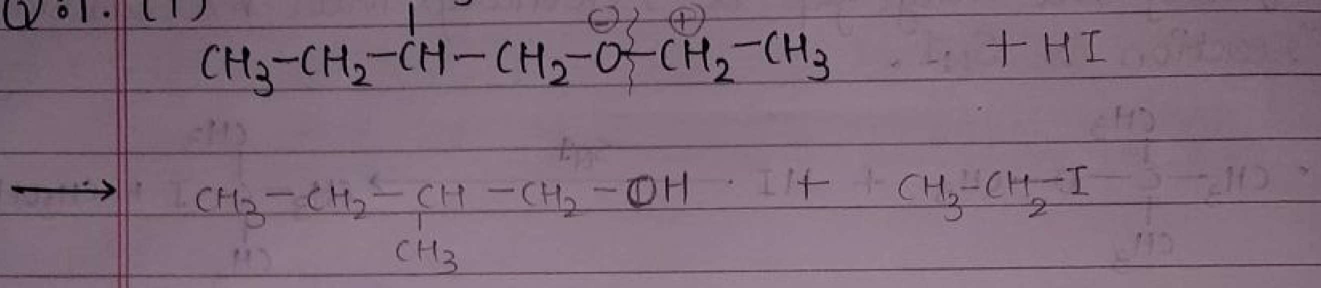
$$CH_3-O-\underset{CH_3}{CH}-CH_3 \xrightarrow{HI} \begin{cases} \xrightarrow[(S_N1)]{H_2O} CH_3-\underset{CH_3}{CH}-I + CH_3OH \\ \xrightarrow[(S_N2)]{DMSO} CH_3I + CH_3-\underset{CH_3}{CH}-OH \end{cases}$$

2-Iodo Propane Methanol

Iodomethane

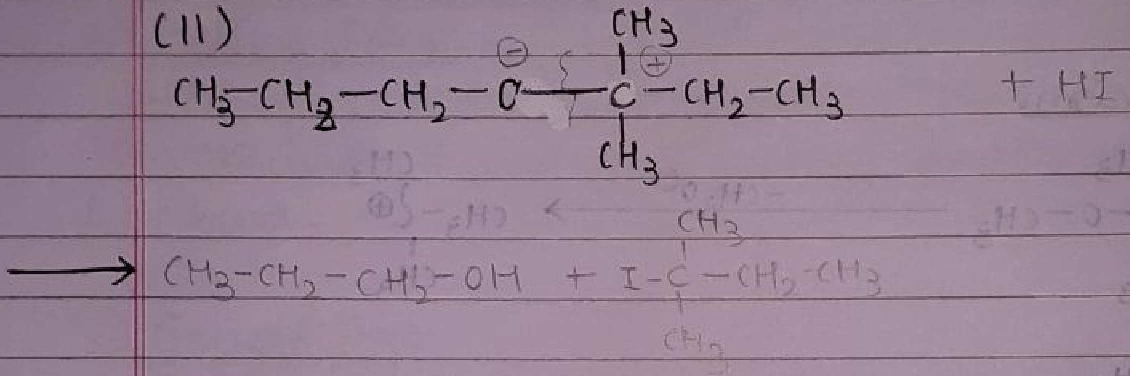
2-Propanol.

Q:1. (I)



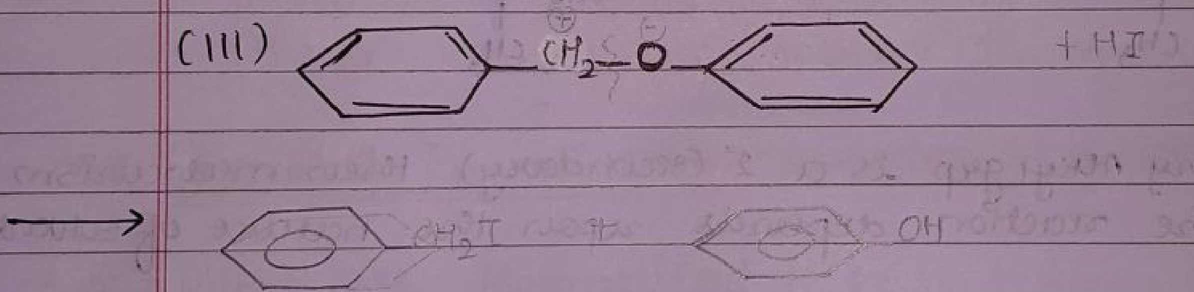
$CH_3-CH_2-\underset{}{\overset{CH_3}{CH}}-CH_2-\overset{\ominus}{O}-\overset{\oplus}{CH_2}-CH_3 + HI \longrightarrow CH_3-CH_2-\underset{CH_3}{CH}-CH_2-OH + CH_3-CH_2-I$

(II)



$CH_3-CH_2-CH_2-\overset{\ominus}{O}-\underset{CH_3}{\overset{CH_3}{\overset{\oplus}{C}}}-CH_2-CH_3 + HI \longrightarrow CH_3-CH_2-CH_2-OH + I-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_3$

(III)



B.) Rxn with hot concentrated HI: (excess)

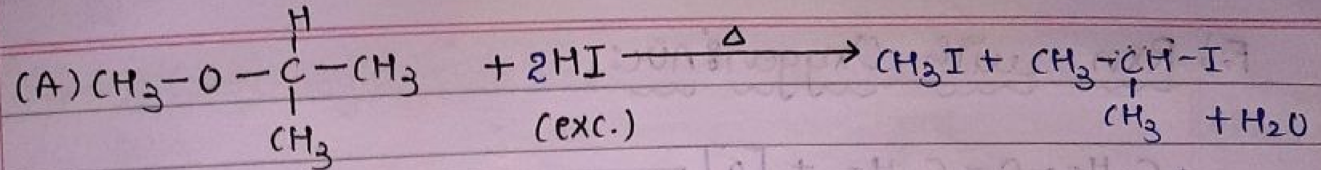
- $CH_3-O-CH_3 + \underset{(excess)}{HI} \xrightarrow{\Delta} CH_3I + CH_3OH$

↳ $CH_3OH + HI \longrightarrow CH_3I + H_2O$

∴ $CH_3-O-CH_3 + 2HI \longrightarrow 2CH_3I + H_2O$

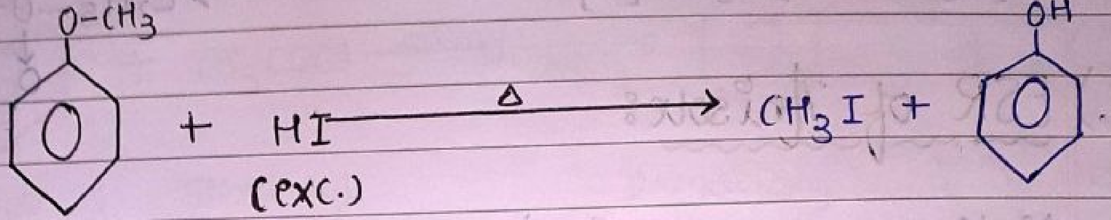
- $CH_3-O-C_2H_5 + \underset{(exc.)}{2HI} \xrightarrow{\Delta} CH_3I + C_2H_5I + H_2O$.

Q:2 (A)



$$CH_3-O-\overset{H}{\underset{CH_3}{C}}-CH_3 + \underset{(exc.)}{2HI} \xrightarrow{\Delta} CH_3I + CH_3-\underset{CH_3}{CH}-I + H_2O$$

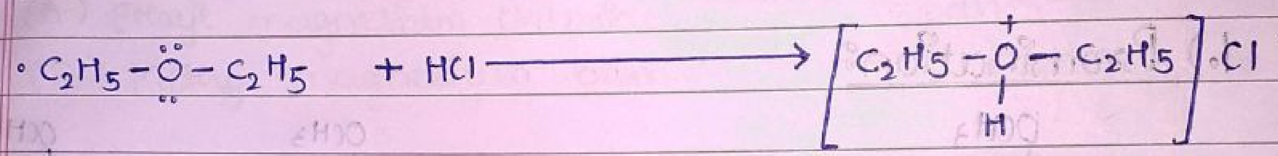
(B)



$$\text{(anisole)} + \underset{(exc.)}{HI} \xrightarrow{\Delta} CH_3I + \text{(phenol)}$$

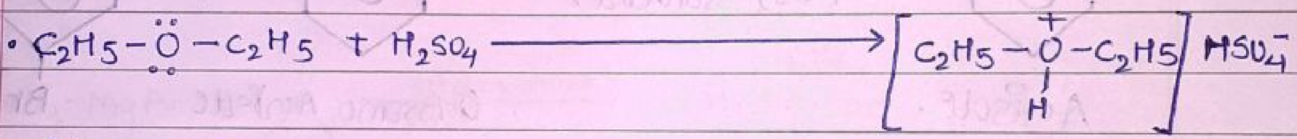
C.) Rxn with HCl and H_2SO_4:

XNCERT



- $C_2H_5-\ddot{O}-C_2H_5 + HCl \longrightarrow \left[C_2H_5-\overset{+}{\underset{H}{O}}-C_2H_5\right]Cl^-$

Ethoxy ethane — Diethyl oxonium chloride



- $C_2H_5-\ddot{O}-C_2H_5 + H_2SO_4 \longrightarrow \left[C_2H_5-\overset{+}{\underset{H}{O}}-C_2H_5\right]HSO_4^-$

Ethoxy ethane — Diethyl oxonium hydrogen sulphate

- Above reaction indicates the basic nature of ether.

D.) Rxn with PCl_5:

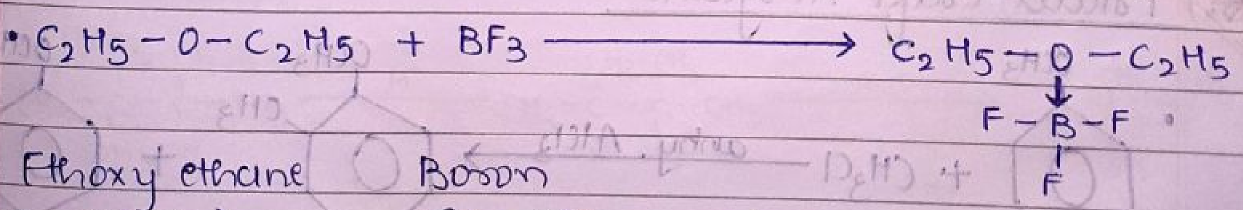
XNCERT

- $C_2H_5-\ddot{O}-C_2H_5 + PCl_5 \longrightarrow POCl_3 + 2C_2H_5Cl$

Ethoxy ethane — Phosph. Oxychloride — Chloro ethane

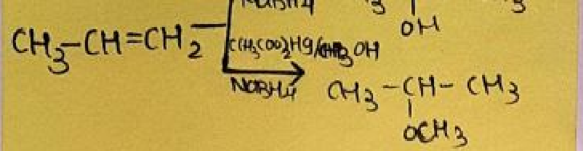
E.) Rxn with BF_3 and $AlCl_3$: (Etherate formed)

XNCERT



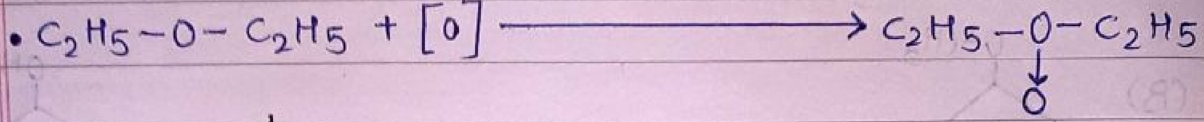
- $C_2H_5-O-C_2H_5 + BF_3 \longrightarrow C_2H_5-\underset{\underset{F-\underset{F}{B}-F}{\downarrow}}{O}-C_2H_5$

Ethoxy ethane (ether) — Boron trifluoride — Diethyl boron trifluoride etherate



Alkoxy mercurious - demercurous rxn

F.) Rxn with Oxygen/Air: (explosive) peroxide formed



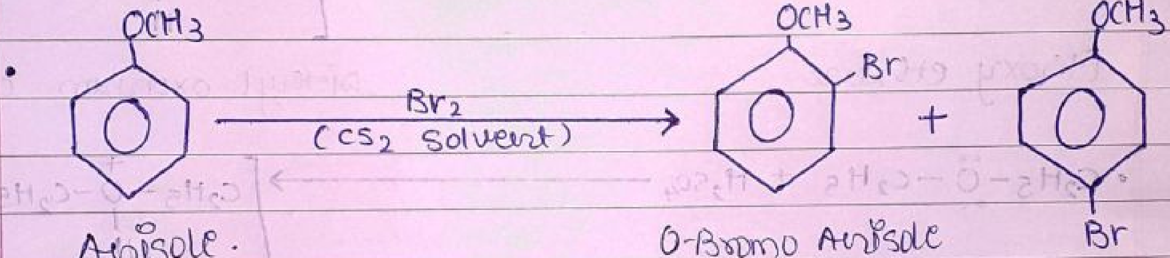
$$\bullet\ C_2H_5-O-C_2H_5 + [O] \longrightarrow C_2H_5-\underset{\downarrow\atop O}{O}-C_2H_5$$

G.) ESR of Anisole:

- Methoxy groups is 'Ortho-para' directing group.

+M dominant over -I [+M group, activated group]

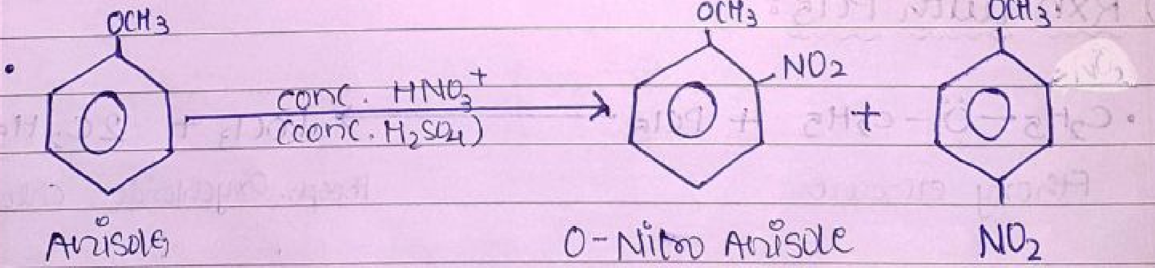
1.) Bromination:



Anisole. O-Bromo Anisole

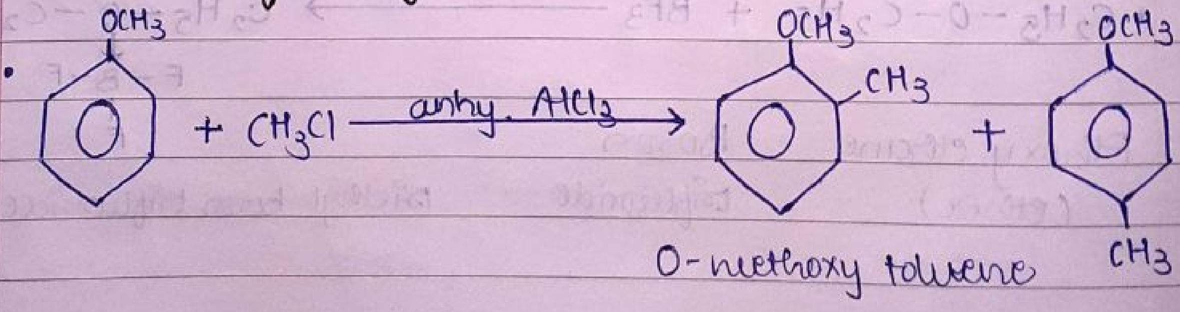
* Br^+ (Bromonium ion) = electrophile.

2.) Nitration:



Anisole O-Nitro Anisole

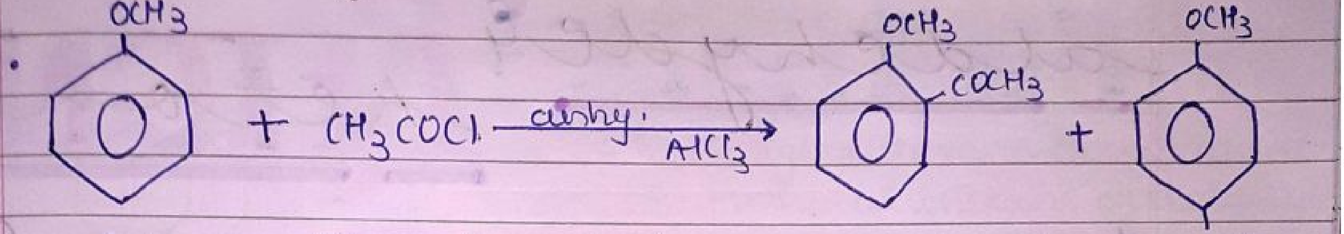
#R 3.) Friedel Craft Alkylation:



O-methoxy toluene

IMP

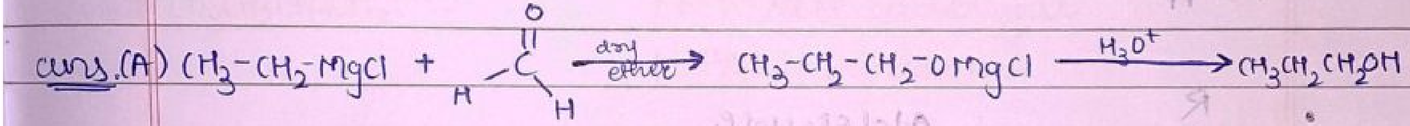
4.) Friedel Craft Acylation:



Anisole + Ethanoyl chloride $\xrightarrow[AlCl_3]{anhy.}$ 2-methoxy acetophenone + 4-methoxy acetophenone

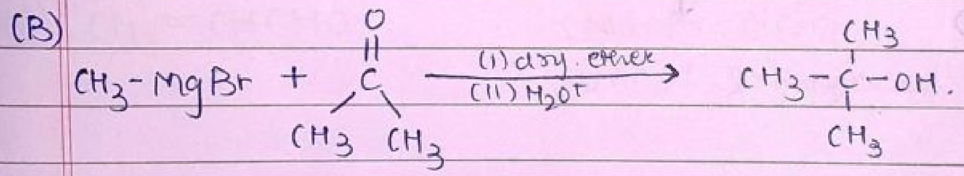
Q:3 (A) Ethyl magnesium chloride ⟶ Propan-1-ol.
(B) Methyl magnesium bromide ⟶ 2-Methyl propan-2-ol

ans.(A)



$$CH_3-CH_2-MgCl + H-\overset{\overset{O}{||}}{C}-H \xrightarrow[ether]{dry} CH_3-CH_2-CH_2-OMgCl \xrightarrow{H_3O^+} CH_3CH_2CH_2OH$$

(B)



$$CH_3-MgBr + CH_3-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow[(II)\ H_2O^+]{(I)\ dry.\ ether} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH.$$

29/08

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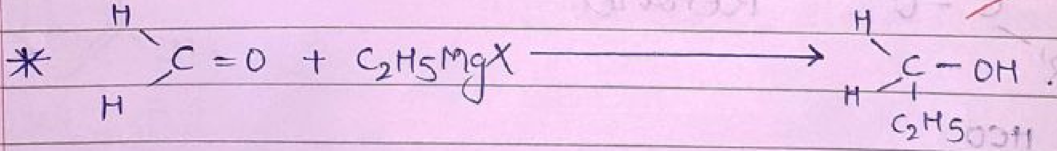
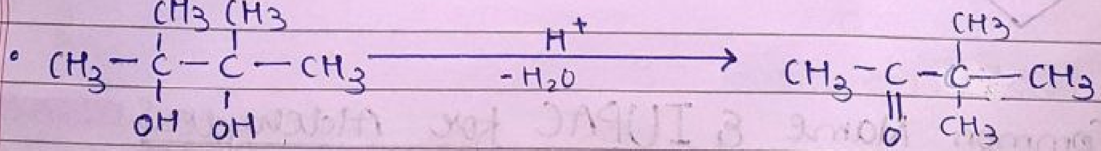


$$H_2C=O + C_2H_5MgX \longrightarrow H_2\underset{C_2H_5}{C}-OH$$

H.) Pinacole - Pinacolone Rxn:

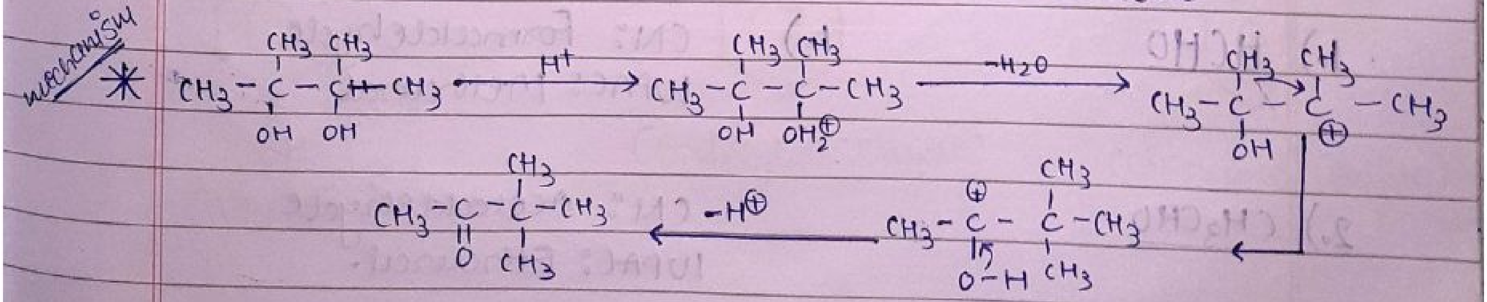


$$CH_3-\overset{CH_3}{\underset{OH}{C}}-\overset{CH_3}{\underset{OH}{C}}-CH_3 \xrightarrow[-H_2O]{H^+} CH_3-\underset{\underset{O}{||}}{C}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

Pinacole Pinacolone

mechanism

*

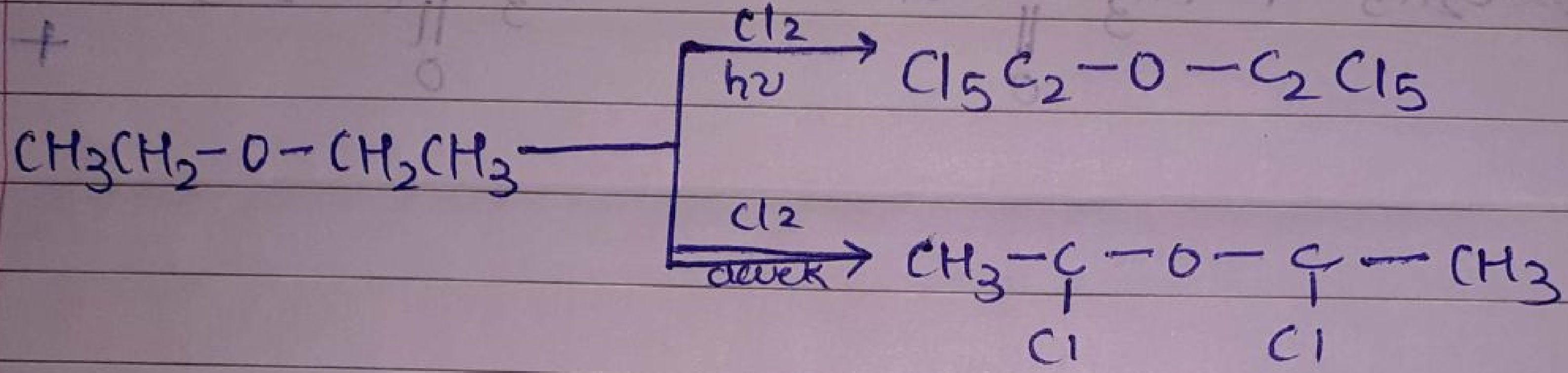


$$CH_3-\overset{CH_3}{\underset{OH}{C}}-\overset{CH_3}{\underset{OH}{C}}-CH_3 \xrightarrow{H^+} CH_3-\overset{CH_3}{\underset{OH}{C}}-\overset{CH_3}{\underset{OH_2^{\oplus}}{C}}-CH_3 \xrightarrow{-H_2O} CH_3-\overset{CH_3}{\underset{OH}{C}}-\overset{CH_3}{\underset{\oplus}{C}}-CH_3$$

$$CH_3-\overset{CH_3}{\underset{\underset{O}{||}}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xleftarrow{-H^{\oplus}} CH_3-\overset{\oplus}{\underset{\underset{O-H}{||}}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

* Halogenation of ether: (chlorination)

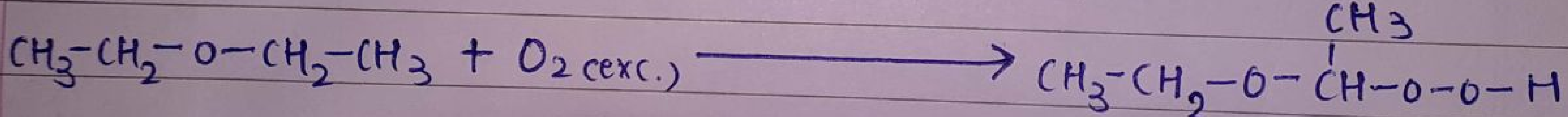
Q



$$CH_3CH_2-O-CH_2CH_3 \xrightarrow[h\nu]{Cl_2} Cl_5C_2-O-C_2Cl_5$$

$$CH_3CH_2-O-CH_2CH_3 \xrightarrow[dark]{Cl_2} CH_3-\underset{Cl}{\underset{|}{C}}-O-\underset{Cl}{\underset{|}{C}}-CH_3$$

* Oxidation of ether: (excess of O_2 / Air)



$$CH_3-CH_2-O-CH_2-CH_3 + O_{2\,(exc.)} \longrightarrow CH_3-CH_2-O-\overset{CH_3}{\overset{|}{C}}H-O-O-H$$

Hydro peroxide

* Ziesel's method: (rxn with cold HI).