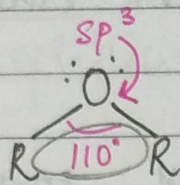
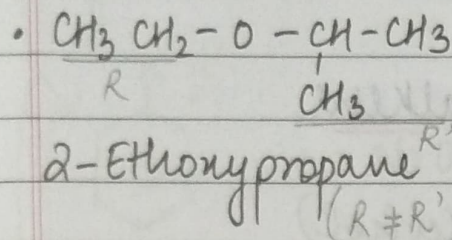




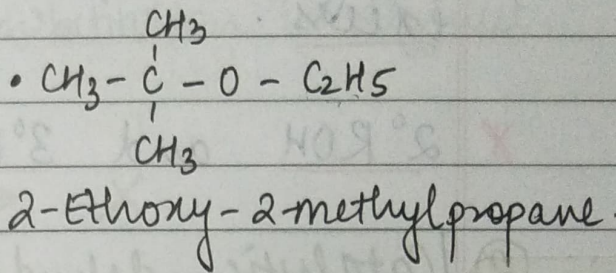
Handwritten Notes  
On  
Ethers

# ETHERS

• Simple ( $R = R'$ )



• Mixed ( $R \neq R'$ )



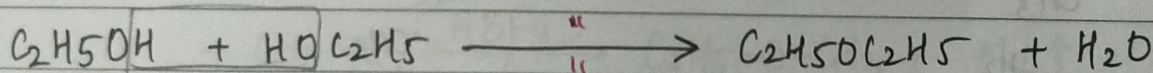
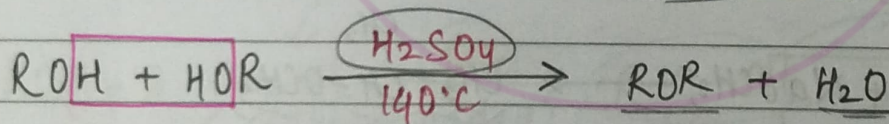
• Isomerism  $\longrightarrow$  functional [ $\text{C}_n\text{H}_{2n+2}\text{O}$ ]  
 $\longrightarrow$  Metamerism  
 $\longrightarrow$  chain

## Preparation

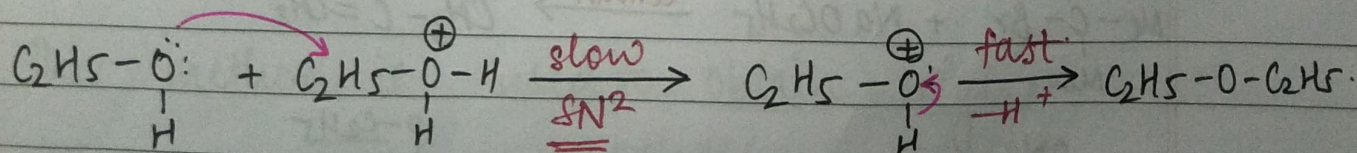
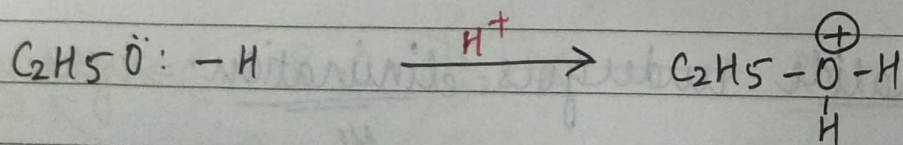
① Dehydration of alcohol

- Acid catalysed dehydration  
 (only simple ethers)

- Intermolecular dehydration



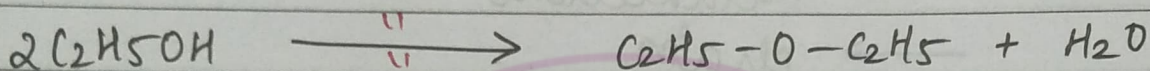
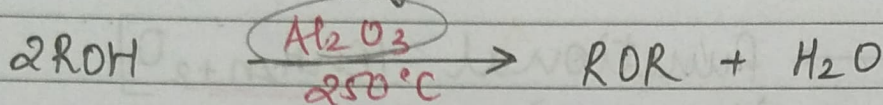
Mechanism :-



\* Only 1° alcohols give ether when taken in excess.

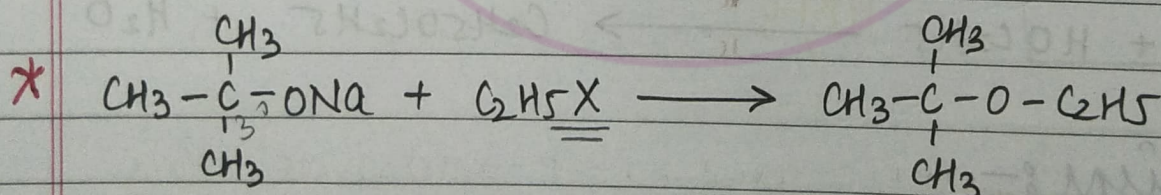
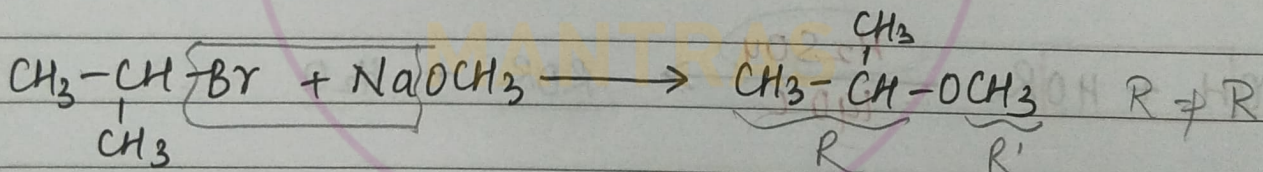
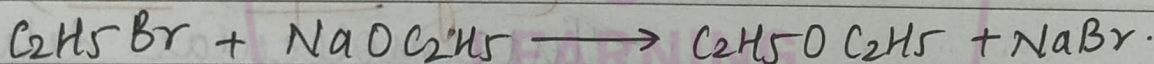
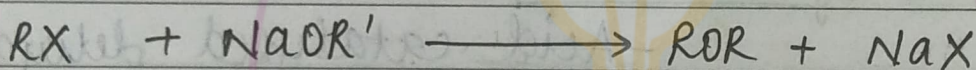
\* 2° ROH and 3° ROH form alkene

② Catalytic dehydration (of alcohol)

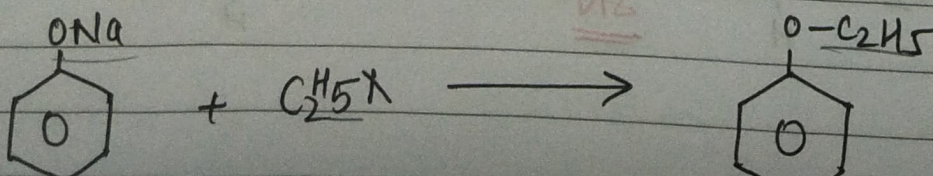
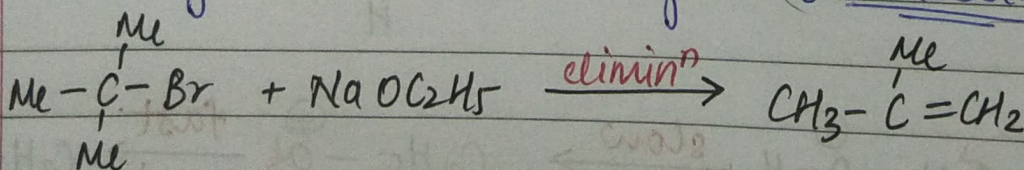


③ Williamson's synthesis

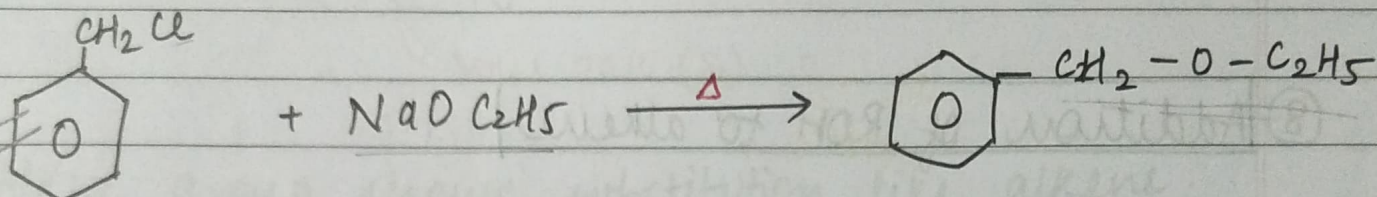
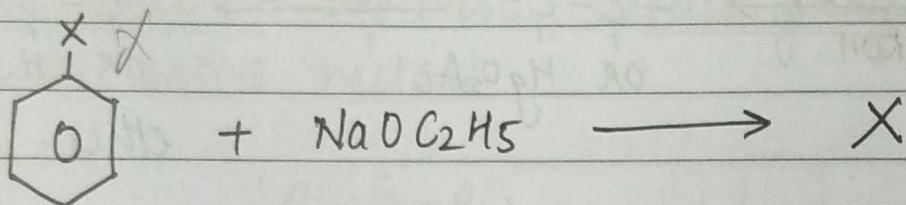
(proper mixed ethers) - Nucleophilic substitution.



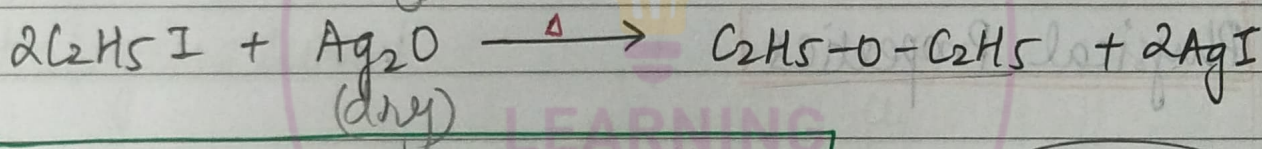
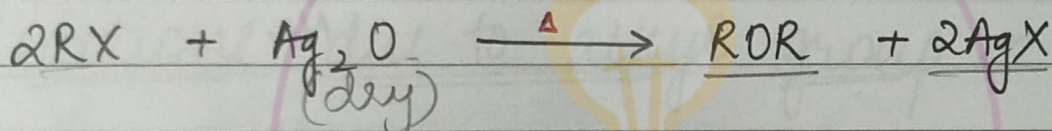
\* 3° alkyl halide undergoes elimination  $\Rightarrow$  alkene



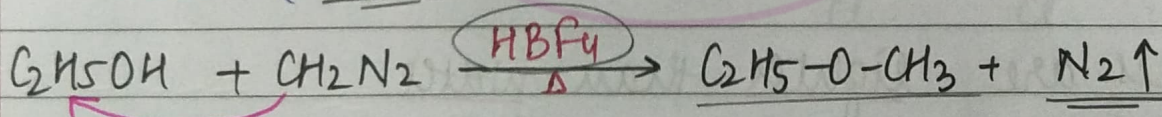
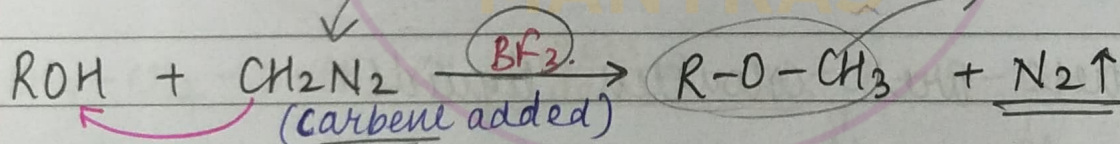
\* Acyl halides cannot be used in Williamson's synthesis as nucleophilic substitution is difficult.



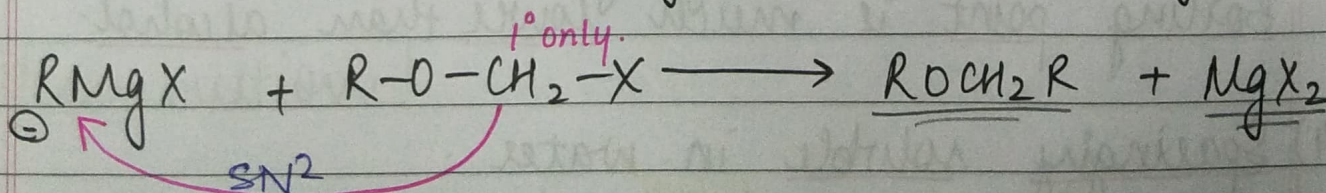
④ Heating RX w/ dry Ag<sub>2</sub>O (only simple ethers)



⑤ From diazomethane & alcohol - only methoxy ethers

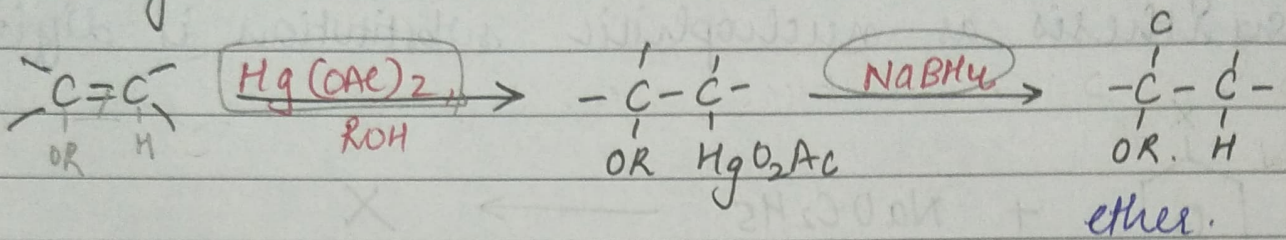


⑥ Reaction w/ lower halogenated ethers & RMgX

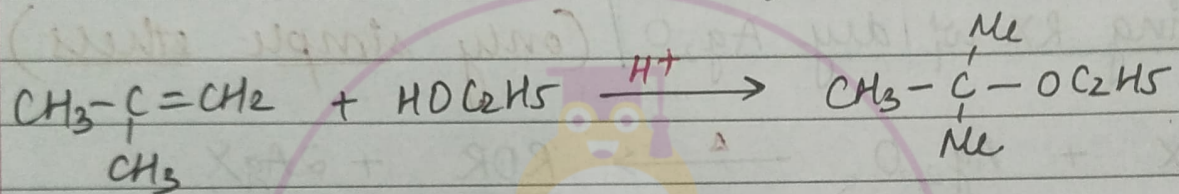
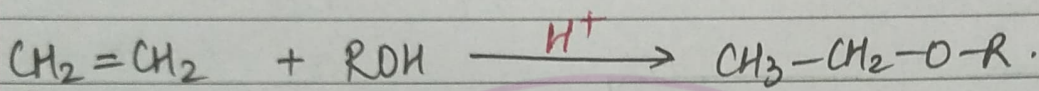


This method is used to obtain higher ethers

## ⑦ Alkyl-mercuration - demercuration



## ⑧ Addition of ROH to alkene



## → Physical Properties

(1)  $\text{CH}_3-\text{O}-\text{CH}_3$ ,  $\text{C}_2\text{H}_5-\text{O}-\text{CH}_3 \rightarrow$  gases.

all others are colourless liquids.

(2) Ethers are lighter than water.

(3) Lower ethers are highly volatile.

Boiling point is much lower than alcohol.

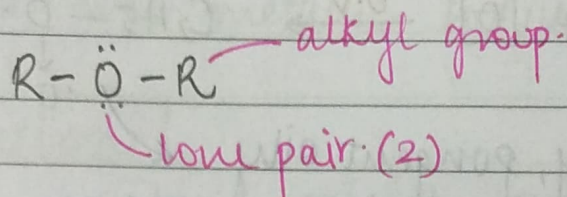
(4) Sparsely soluble in water.

Easily soluble in organic solvents.

(5) Chemically less reactive.

## → Chemical Properties

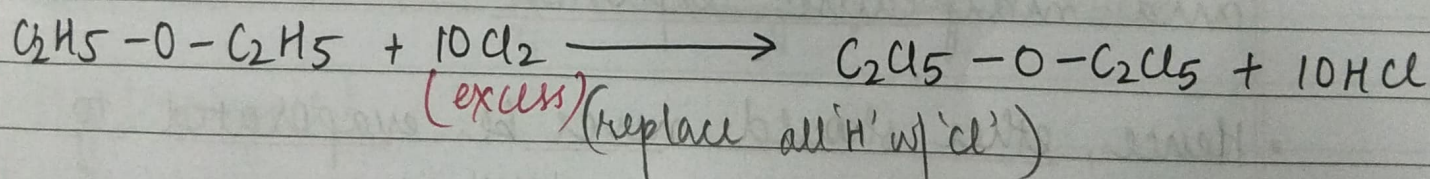
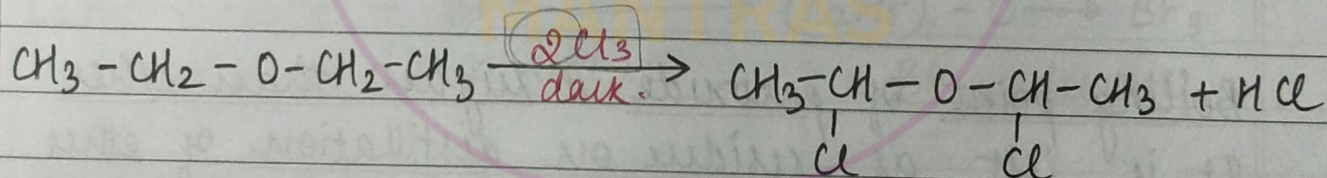
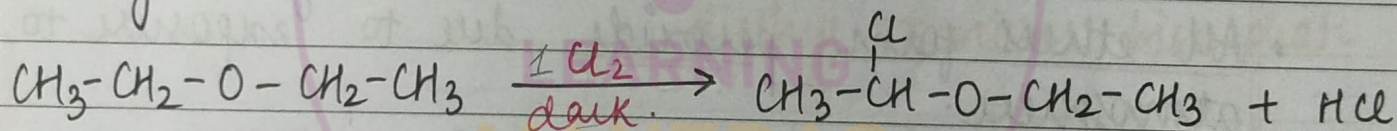
- No reaction w/ base, oxidising agents, reducing agents and active metals.



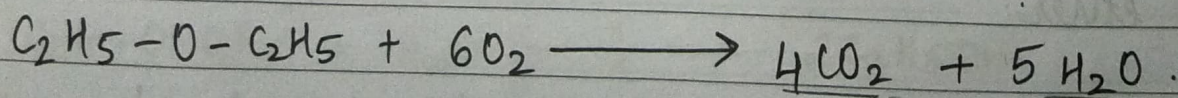
- Alkyl group shows substitution like alkene.
- 2 lone pairs form salts w/ acids.
- C-O bond fission is possible w/ acids.

## \* Reactions due to alkyl group :-

### ① Halogenation



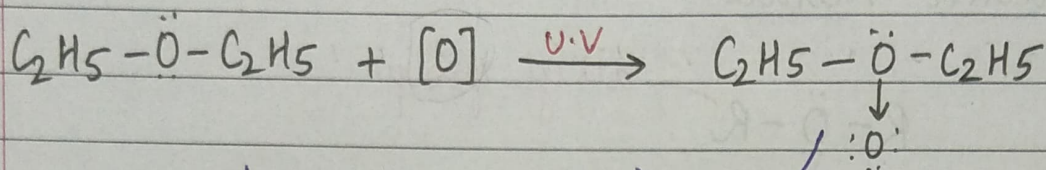
### ② Combustion



(normal combustion to air, carbon-dioxide & water)

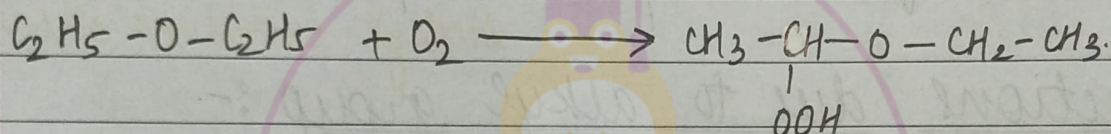
\* Reaction due to ethral oxygen :-

① Oxidation and peroxide formation



heavy, pungent oily liquid; decomposes on heating.

On long contact w/ air :-



peroxide of diethyl ether.

• All ethers form peroxide due to exposure to atmosphere.

• Boiling point of peroxide is higher than ether. It is left as residue on distillation of ether and may cause explosion.

• Hence, ether should never be evaporated to dryness.

It is essential to remove peroxide before distilling the ether.

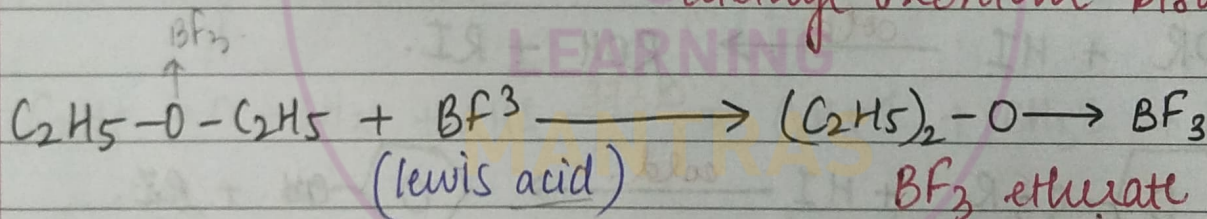
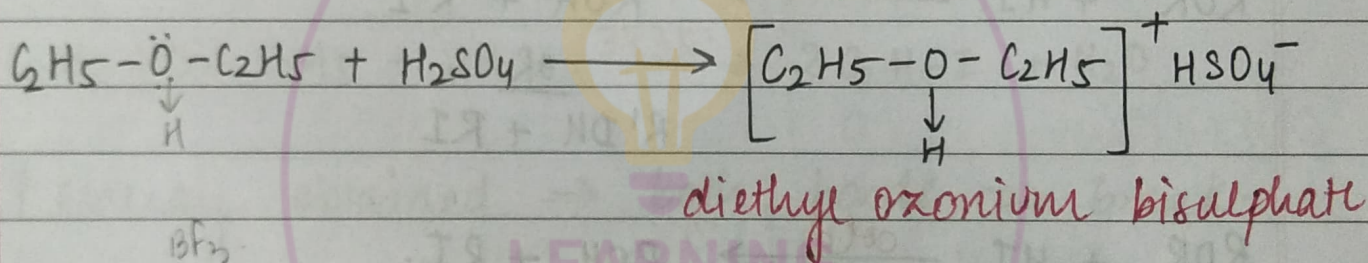
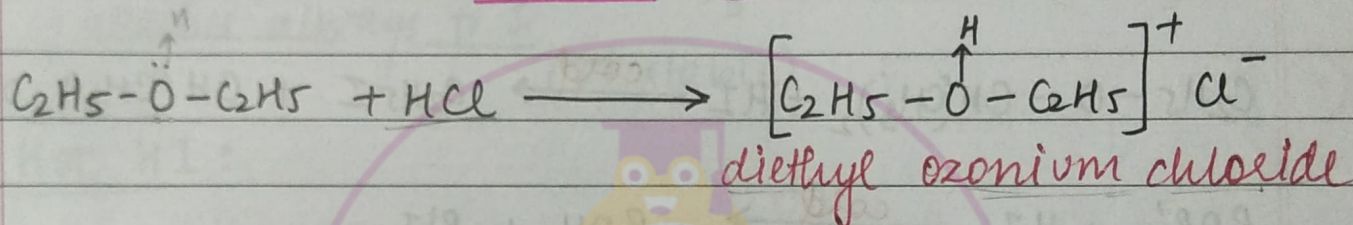
\* Ethers can be freed from peroxide by shaking w/ ferrous salt solutions or distilling w/ conc. H<sub>2</sub>SO<sub>4</sub>

- Ethers used as a solvent is dry ether. This is called absolute ether and can be prepared by distillation of ordinary ethers from conc. sulphuric acid.

It is stored over metallic sodium. (Na)

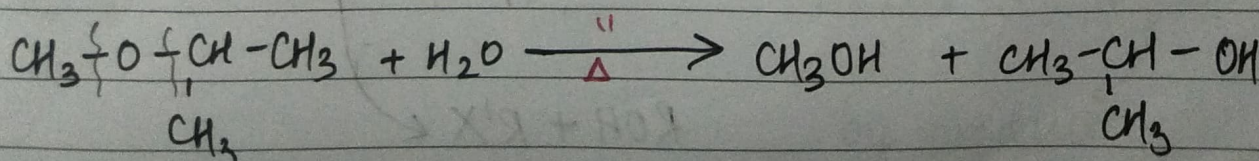
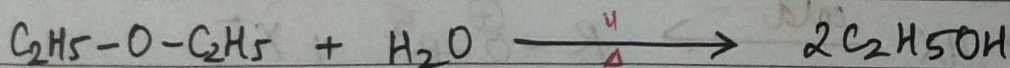
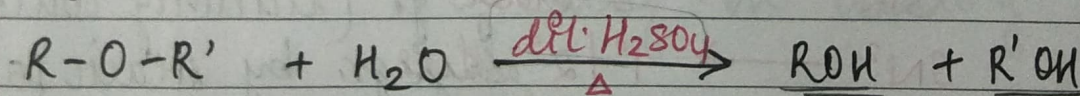
## ② Salt formation

- lone pair of oxygen acts as lewis/bronsted lowri base



\* Reactions involving breaking of -C-O bond :-

## ① Hydrolysis



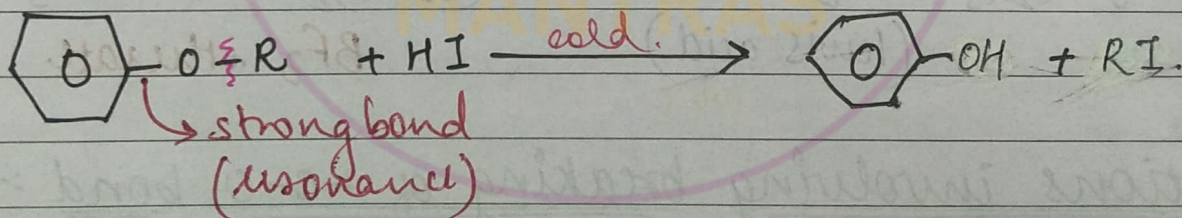
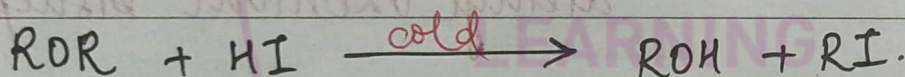
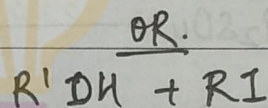
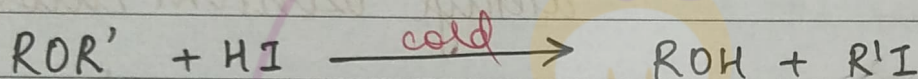
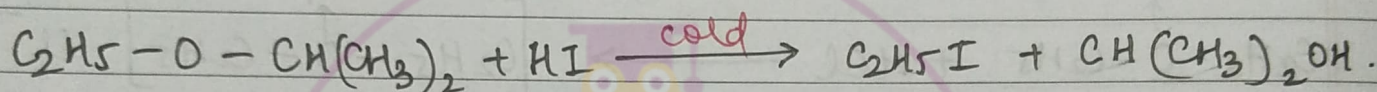
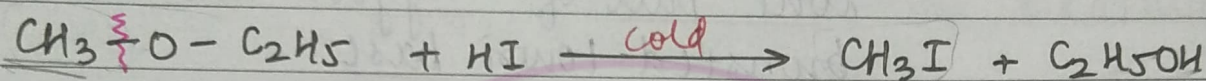


## ② Action of HI

- Temperature dependant

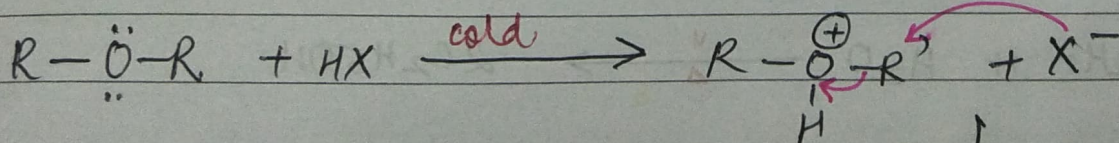
(i) Cold HI: (forms iodide + alcohol)

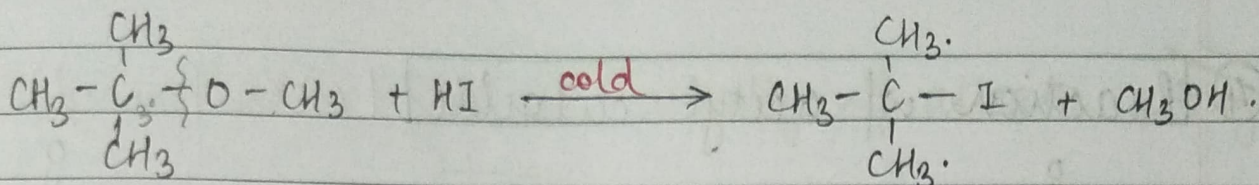
\* For ethers w/ 1° & 2° alkyl groups, Iodine always prefers smaller alkyl group. (3° → larger group)



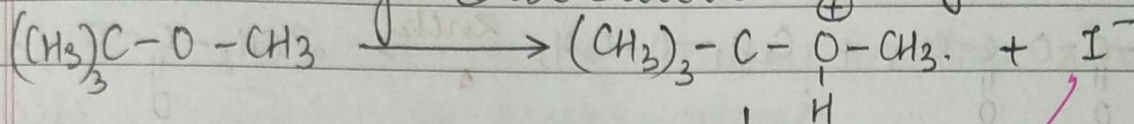
Mechanism:-

$\text{S}_\text{N}^1$  → 3° alkyl gr. (reactivity controlled)  
 $\text{S}_\text{N}^2$  → 1°/2° alkyl gr. by steric factors

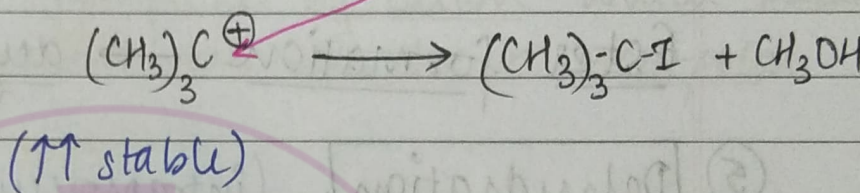




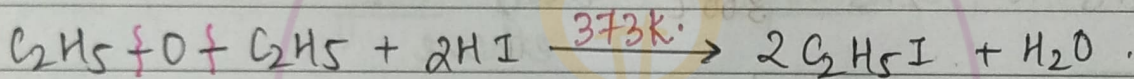
SN1 Controlled by carbocation stability



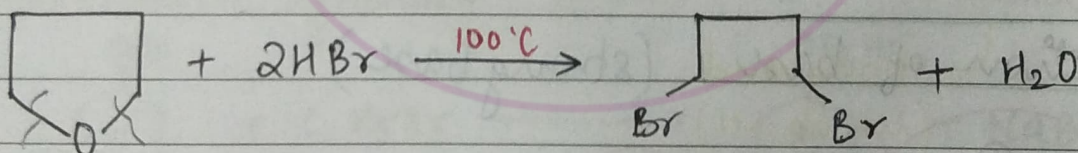
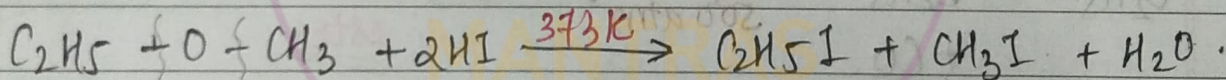
3° carbocation  
attaches always to I



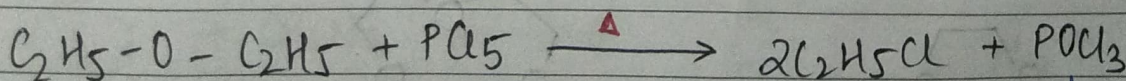
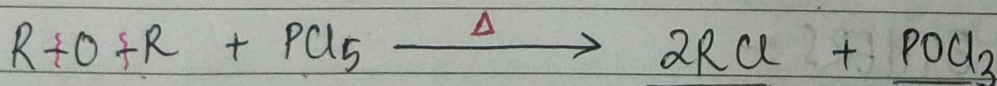
(ii) Hot HI:



↑ energy obtained ⇒ both bonds can break.

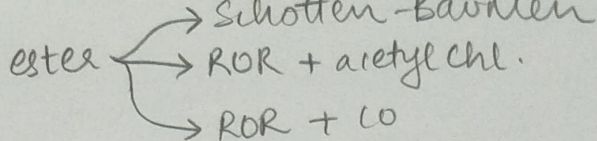


③ Reaction w/ PCl<sub>5</sub> (halide + POCl<sub>3</sub>)  
- only on heating.

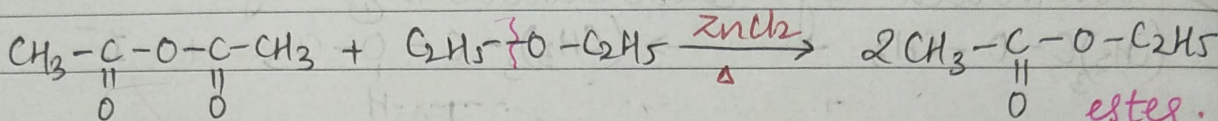
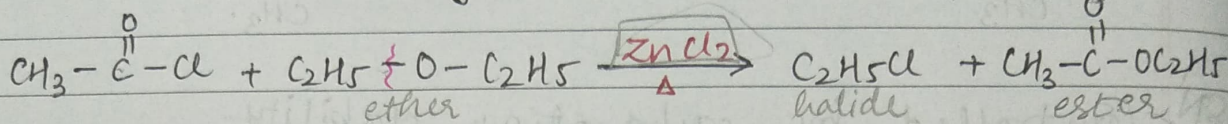


by product

phosphorus oxychloride



④ Reaction of acetyl chloride (ester formed)

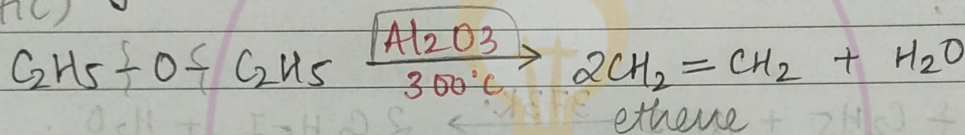


(breaking of bond  $\rightarrow$  same rules as HI.)

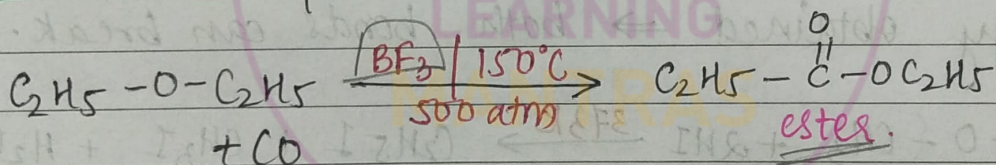
Ester formation  $\rightarrow$  acylation.

⑤ Dehydration (intramolecular)

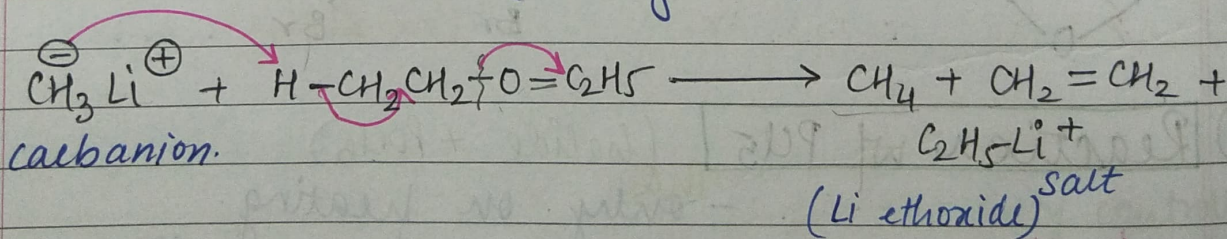
(catalytic)



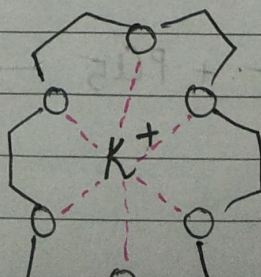
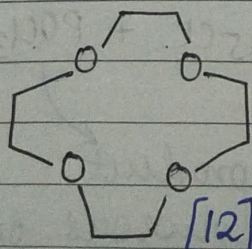
⑥ Reaction w/ CO



⑦ Action of base (strong base)



\* CROWN ETHERS :-

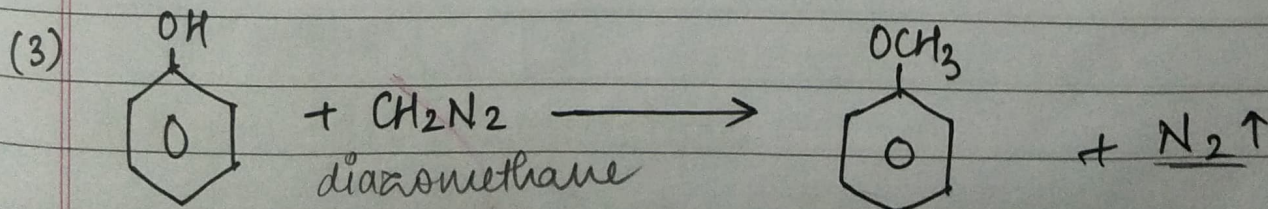
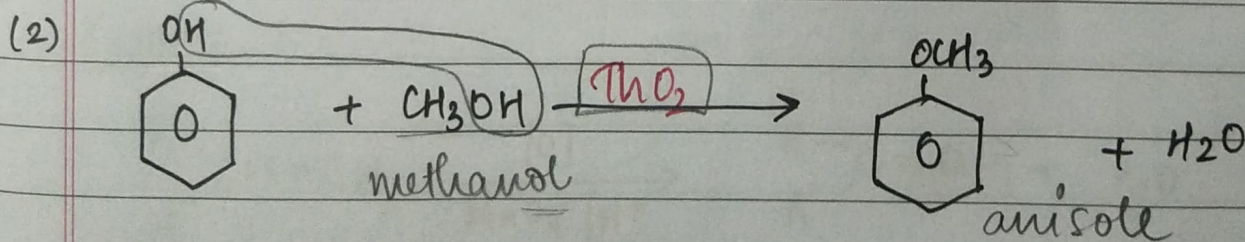
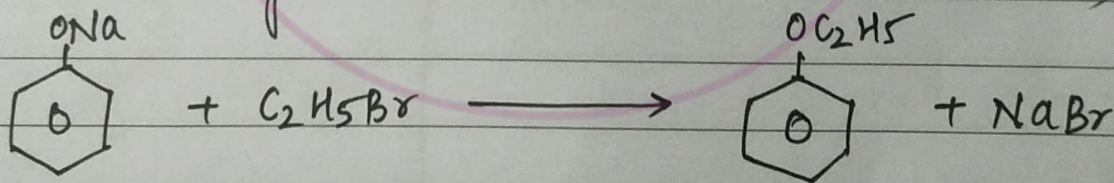


- Heterocyclic, polyethers usually w/ at least 4 oxygen atoms
- Names consist of 2 numbers:
  - (i) Total no. of atoms in the ring [ ]
  - (ii) No. of oxygen atoms.
- Crown ethers form complexes w/ cation. which makes an ionic compound which can dissolve in non-polar organic solvents.
- These complexes are called inclusion compounds or host (ether) - guest (cation) compound.

### \* AROMATIC ETHERS :-

#### • preparation -

(1) Williamson's synthesis -  $(RONa + R'X \rightarrow \text{ether})$



Aromatic ethers undergo EAS mechanism.

