$$CH_3-CH_2-O-CH_2-CH_3 + 2Cl_2 \xrightarrow{\text{sunlight}} CH_3-\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{\underset{|}{\overset{|}{C}}}}-O-\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{\underset{|}{\overset{|}{C}}}}-CH_3$$ ($\alpha\alpha, \alpha^1\alpha^1$ –tetrachloro diethyl ether)

In dark the two α - hydrogens are substituted by two chlorines on reaction with chlorine.

2) with air : Diethyl ether when exposed to air forms a mixture due to the formation of diethyl peroxide.

$$C_2H_5-O-C_2H_5 + \frac{1}{2}O_2 \rightarrow \underset{\text{(explosive)}}{C_2H_5-O-O-C_2H_5}$$ (or) $C_2H_5-\underset{\displaystyle O}{\overset{\displaystyle \downarrow}{O}}-C_2H_5$ It is

freed from peroxide by treating with ferrous sulphate.

3) with dil.H_2SO_4 : Diethyl ether is hydrolysed to ethyl alcohol in presence of sulphuric acid

$$C_2H_5-O-C_2H_5 + H-OH \xrightarrow{\text{dil.}H_2SO_4} 2C_2H_5OH$$

4) with cold and conc. mineral acids.

Ether reacts with cold and conc. mineral acids like HCl, H_2SO_4, HNO_3 etc. to form oxonium salts. Formation of these oxonium salts with the mineral acids is the indication of its basic nature.

$$(C_2H_5)_2\ddot{O} + HCl \rightarrow (C_2H_5)_2OH^+Cl^-$$ (diethyl oxonium chloride)

$$(C_2H_5)_2\ddot{O} + H_2SO_4 \rightarrow \left[(C_2H_5)_2OH\right]_2^+SO_4^{-2}$$

(diethyl oxonium sulphate)

5) with HI: With cold HI, one C – O bond is cleaved and the products are ethyl alcohol and ethyl iodide. $C_2H_5-O-C_2H_5 + HI \rightarrow C_2H_5-OH + C_2H_5-I$

- With hot and excess of HI , both C – O bonds are cleaved and two moles of $C_2H_5 - I$ are formed
  $C_2H_5-O-C_2H_5 + 2HI \rightarrow 2C_2H_5-I + H_2O$
- In case of mixed ethers the HI is added to smaller alkyl group.
  $CH_3-O-C_2H_5 + HI \rightarrow CH_3-I + C_2H_5-OH$
- Ziesel's method is useful to detect and estimate the number of methoxy groups present in the given ether.
- The reaction of ether with HI forms the basis for Ziesel's method.

6) with PCl_5 : with PCl_5 diethyl ether gives ethylchloride

$$C_2H_5-O-C_2H_5 + PCl_5 \xrightarrow{\Delta} 2C_2H_5Cl + POCl_3$$

7) Dehydation : on dehydration in the presence of alumina diethyl ether gives ethylene.

$$C_2H_5-O-C_2H_5 \xrightarrow[360^0C]{\text{an.}Al_2CO_3} 2C_2H_4 + H_2O$$

8) with CO: In the presence of BF_3 at 150°C and 500 atm pressure diethyl ether reacts with CO and forms ethyl propionate (Ester)

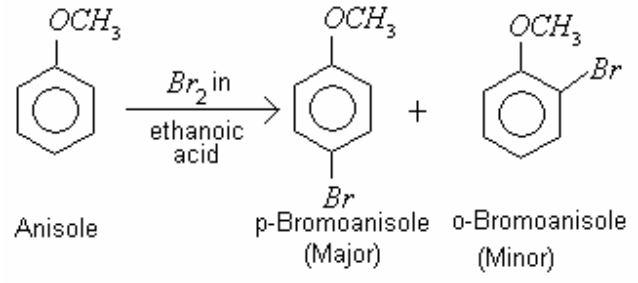
$$C_2H_5-O-C_2H_5 + CO \xrightarrow[500\text{ atm}]{BF_3, 150^0C} C_2H_5-COOC_2H_5$$ (ethyl propionate)

9) Reduction : Diethyl ether reduces to ethane on reduction with Na/liq.NH_3.

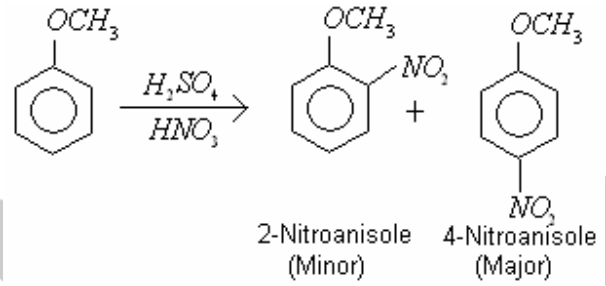
$$C_2H_5-O-C_2H_5 + 2H \xrightarrow{Na/liq.NH_3} C_2H_6 + C_2H_5OH$$

ELECTROPHILIC SUBSTITUTION.

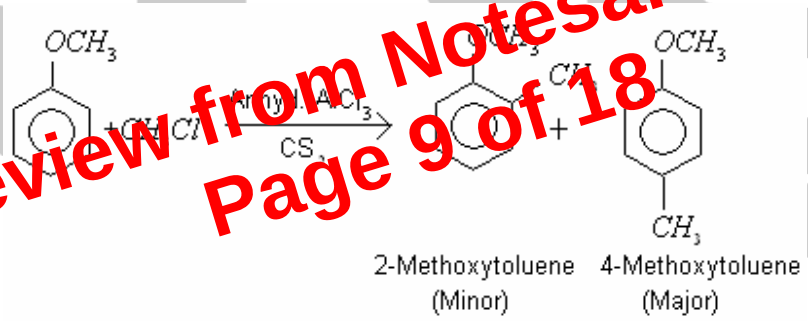
1) **HALOGENATION**:

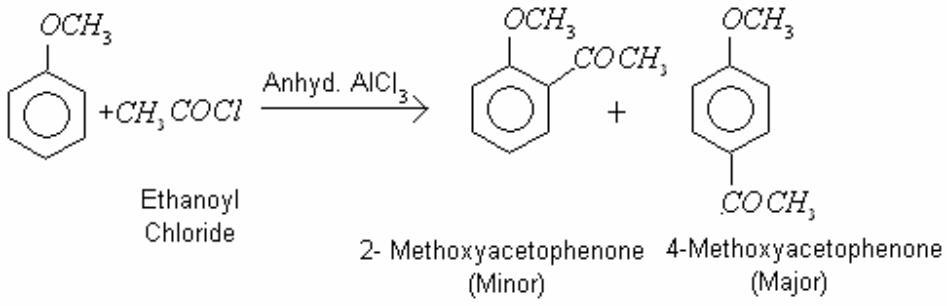


2) **NITRATION**:



3) **FRIEDEL-CRAFTS REACTION:**





MECHANISM OF DEHYDRATION :

It takes place in three steps :

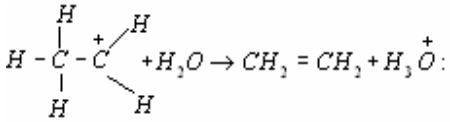
i) $CH_3-CH_3-OH+H_2SO_4 \Leftrightarrow$

$$CH_3-CH_2-{}^{+}\underset{\underset{H}{|}}{\overset{\cdot\cdot}{O}}-H+\overline{OSO_3H}$$

ii) Formation of carbonation. It is the slowest step or rate determining step.

$$CH_3-CH_2-{}^{+}\underset{\underset{H}{|}}{\overset{\cdot\cdot}{O}}-H \Leftrightarrow CH_3-\overset{+}{C}H_2+H_2\overset{\cdot\cdot}{O}:$$

iii) Elimination of proton to get alkene



Since the rate determining step is the formation of carbocation, the rate of dehydration is directly proportional to the formation of carbocation. Since the stability of carbocation is $3^0 > 2^0 > 1^0$, the order of dehydration of alcohols is

$(CH_3)_3COH > (CH_3)_2CHOH > CH_3-CH_2OH$

Dehydration of alcohol requires 95% H_2SO_4 at $H_2SO_4 170^0C$, 2^0 alcohol requires 75% H_2SO_4 at 100^0, where 3^0 as alcohol requires 5% H_2SO_4 at 50^0C .

- The dehydration of 1^o alcohol goes by E_2 mechanism but that of 2^o and 3^o alcohols go by E_1 mechanism.
  When more than one product is formed, the major product is according to **Zaitsev's** rule. It states that hydrogen is removed from $\beta-carbon$ that is bonded to the least number of hydrogen atoms.(**β-elimination**)
  Eg. Dehydration of 2-butanol predominantly gives 2-butene.

  $$CH_3-CH_2-CHOH-CH_3 \xrightarrow[H_2SO_4]{Conc}$$

  $$CH_3-CH=CH-CH_3+CH_3-CH_2-CH=CH_2$$

  2-butene(major) 1-butene (minor)
- **FORMATION OF ADDTION COMPOUNDS :** Ethyl alcohol reacts with anhydrous metal salts to form addition compounds (that is alcohol of crystallisation)
  a) $C_2H_5OH.3CaCl_2, C_2H_5OH.6MgCl_2, C_2H_5OH.3CuSO_4$

USES OF SOME IMPROTANT COMPOUNDS

(Methanol and ethanol)

METHANOL

1. Methanol a colourless liquid with b.pt 67^0C .is used as solvent, paints, varnishes, shellac etc.,
2. Used in the manfacture of HCHO, perfumes and dyes.
3. Used in the preparation of methylated spirt, a mixture of recatified spirit (95.6% ethyl alcohol + 4.4%water) and methyl alcohol making ethyl alcohol unfit for drinking .
4. Two types of methylated spirits:
   a) mineralised spirit = 90% rectified spirit + 9% methyl alcohol + 1% pyridine