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.

\[
\begin{align*}
C_2H_5 - O - C_2H_5 + \frac{1}{2}O_2 &\rightarrow C_2H_5 - O - O - C_2H_5 \\
\text{or} &\rightarrow C_2H_5 - O - C_2H_5
\end{align*}
\]

It is freed from peroxide by treating with ferrous sulphate.

3) with dil. H₂SO₄: Diethyl ether is hydrolysed to ethyl alcohol in presence of sulphuric acid.

\[
C_2H_5 - O - C_2H_5 + H - OH \rightarrow 2C_2H_5OH
\]

4) with cold and conc. mineral acids.

Ether reacts with cold and conc. mineral acids like HCl, H₂SO₄, HNO₃ etc. to form oxonium salts. Formation of these oxonium salts with the mineral acids is the indication of its basic nature.

\[
\begin{align*}
(C_2H_5)_2O + HCl &\rightarrow (C_2H_5)_2OH^+Cl^- \\
\text{and} &\rightarrow (C_2H_5)_2O + H_2SO_4 \rightarrow [(C_2H_5)_2OH]_2SO_4^2
\end{align*}
\]

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 C₂H₅ – I are formed.
- In case of mixed ethers, HI is added to smaller alkyl group.
- 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 PCl₅: with PCl₅ diethyl ether gives ethylchloride.

\[
C_2H_5 - O - C_2H_5 + PCl_5 \rightarrow 2C_2H_5Cl + POCl_3
\]

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

\[
C_2H_5 - O - C_2H_5 \rightarrow 2C_2H_4 + H_2O
\]

8) with CO: In the presence of BF₃ at 150°C and 500 atm pressure diethyl ether reacts with CO and forms ethyl propionate (Ester).

\[
C_2H_5 - O - C_2H_5 + CO \rightarrow C_2H_5 - COOC_2H_5 \quad \text{(ethyl propionate)}
\]

9) Reduction: Diethyl ether reduces to ethane on reduction with Na/liq.NH₃.

\[
C_2H_5 - O - C_2H_5 + 2H \rightarrow Na/liq.NH₃ \rightarrow C_2H_6 + C_2H_5OH
\]
ELECTROPHILIC SUBSTITUTION.

1) HALOGENATION:

$$\text{OCH}_3 \xrightarrow{\text{Br}_2 \text{in ethanolic acid}} \begin{cases} \text{OCH}_3 \\ \text{Br}_2 \end{cases} \rightarrow \begin{cases} \text{OCH}_3 \\ \text{Br}_2 \end{cases} + \begin{cases} \text{OCH}_3 \\ \text{Br} \end{cases}$$

Anisole → p-Bromoisooisole (Major) + o-Bromoisooisole (Minor)

2) NITRATION:

$$\text{OCH}_3 \xrightarrow{\text{H}_2\text{SO}_4, \text{HNO}_3} \begin{cases} \text{OCH}_3 \\ \text{NO}_2 \end{cases} \rightarrow \begin{cases} \text{OCH}_3 \\ \text{NO}_2 \end{cases} + \begin{cases} \text{OCH}_3 \\ \text{NO}_2 \end{cases}$$

2-Nitroanisole (Minor) + 4-Nitroisooisole (Major)

3) FRIEDEL-CRAFTS REACTION:

$$\text{OCH}_3 \xrightarrow{\text{AlCl}_3} \begin{cases} \text{OCH}_3 \\ \text{CH}_3 \end{cases} \rightarrow \begin{cases} \text{OCH}_3 \\ \text{CH}_3 \end{cases} + \begin{cases} \text{OCH}_3 \\ \text{CH}_3 \end{cases}$$

2-Methoxytoluene (Minor) + 4-Methoxytoluene (Major)

$$\text{OCH}_3 + \text{CH}_2\text{COCl} \xrightarrow{\text{Anhyd. AlCl}_3} \begin{cases} \text{OCH}_3 \\ \text{COCH}_3 \end{cases} \rightarrow \begin{cases} \text{OCH}_3 \\ \text{COCH}_3 \end{cases} + \begin{cases} \text{OCH}_3 \\ \text{COCH}_3 \end{cases}$$

2-Methoxyacetophenone (Minor) + 4-Methoxyacetophenone (Major)
MECHANISM OF DEHYDRATION:

It takes place in three steps:

i) \[ CH_3 - CH_3 - OH + H_2SO_4 \leftrightarrow CH_3 - CH_2 - O - H + OSO_3H \]

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

\[ CH_3 - CH_2 - O - H \leftrightarrow CH_3 - CH_2 + H_2O \]

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

\( (CH_3)_3 COH > (CH_3)_2 CHOH > CH_3 - CH_2 OH \)

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

- 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. (\( \beta - elimination \))

E.g. Dehydration of 2-butanol predominantly gives 2-butene.

\[ CH_3 - CH_2 - CHOH - CH_3 \rightarrow H_2SO_4 \]

\[ CH_3 - CH = CH - CH_3 + CH_3 - CH_2 - CH = CH_2 \]

2-butene (major) 1-butene (minor)

- FORMATION OF ADDITION 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 IMPORTANT COMPOUNDS

(Methanol and ethanol)

METHANOL

1. Methanol a colourless liquid with b.pt 67\(^\circ\)C is used as solvent, paints, varnishes, shellac etc.
2. Used in the manufacture of HCHO, perfumes and dyes.
3. Used in the preparation of methylated spirit, a mixture of rectified 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