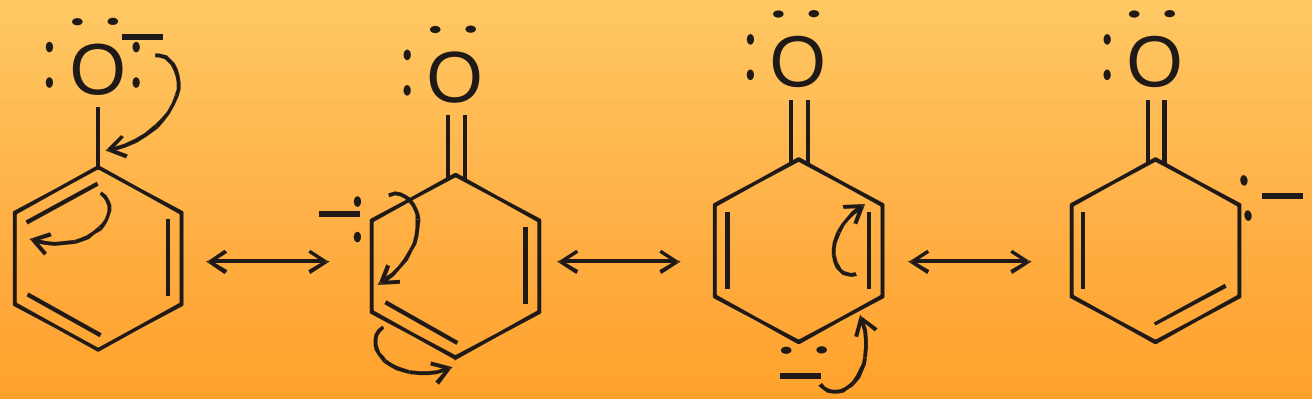
ORGANIC COMPOUNDS CONTAINING OXYGEN - III

Objectives

- Properties of phenols
- Reaction of phenols
- Preparation of ethers
- Properties and reactions of ethers
- Some useful ethers
- Crown ethers

Acidity of phenol

Phenol is more acidic than aliphatic alcohols because conjugate base is stabilized by resonance.



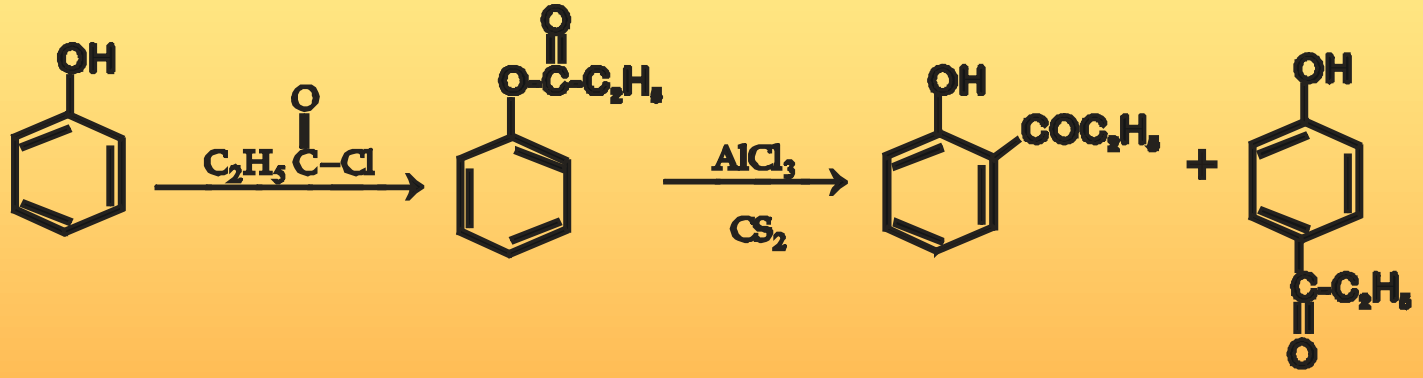
Reactions of phenol

Electrophilic aromatic substitution

—OH group is ortho, para- directing group and activates the benzene rings.

Chemical reaction of phenol

Fries rearrangement

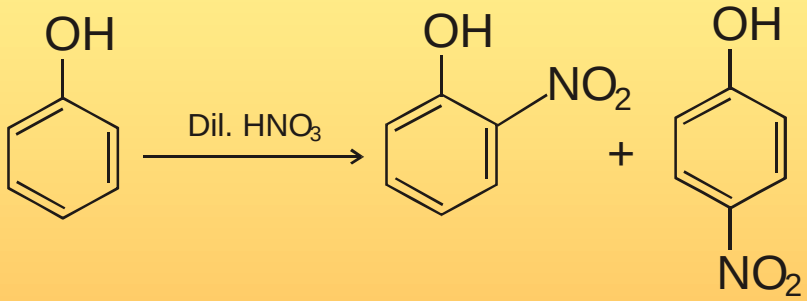


Distillation with Zn dust :

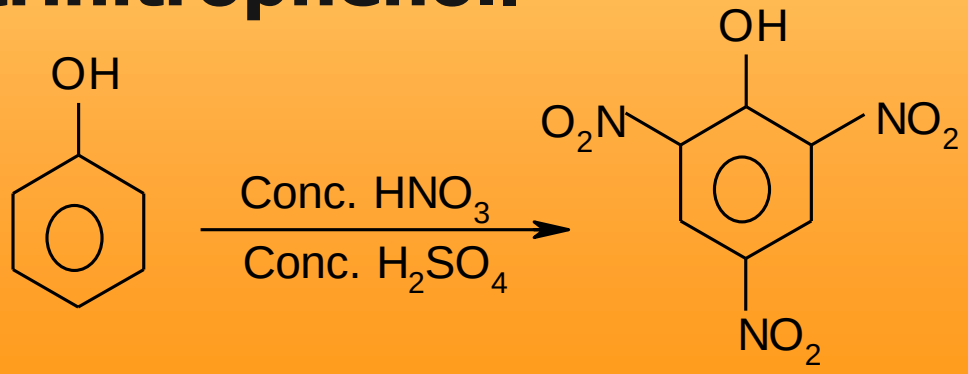
$$C_6H_5OH \xrightarrow{f} C_6H_6 + ZnO$$

Nitration

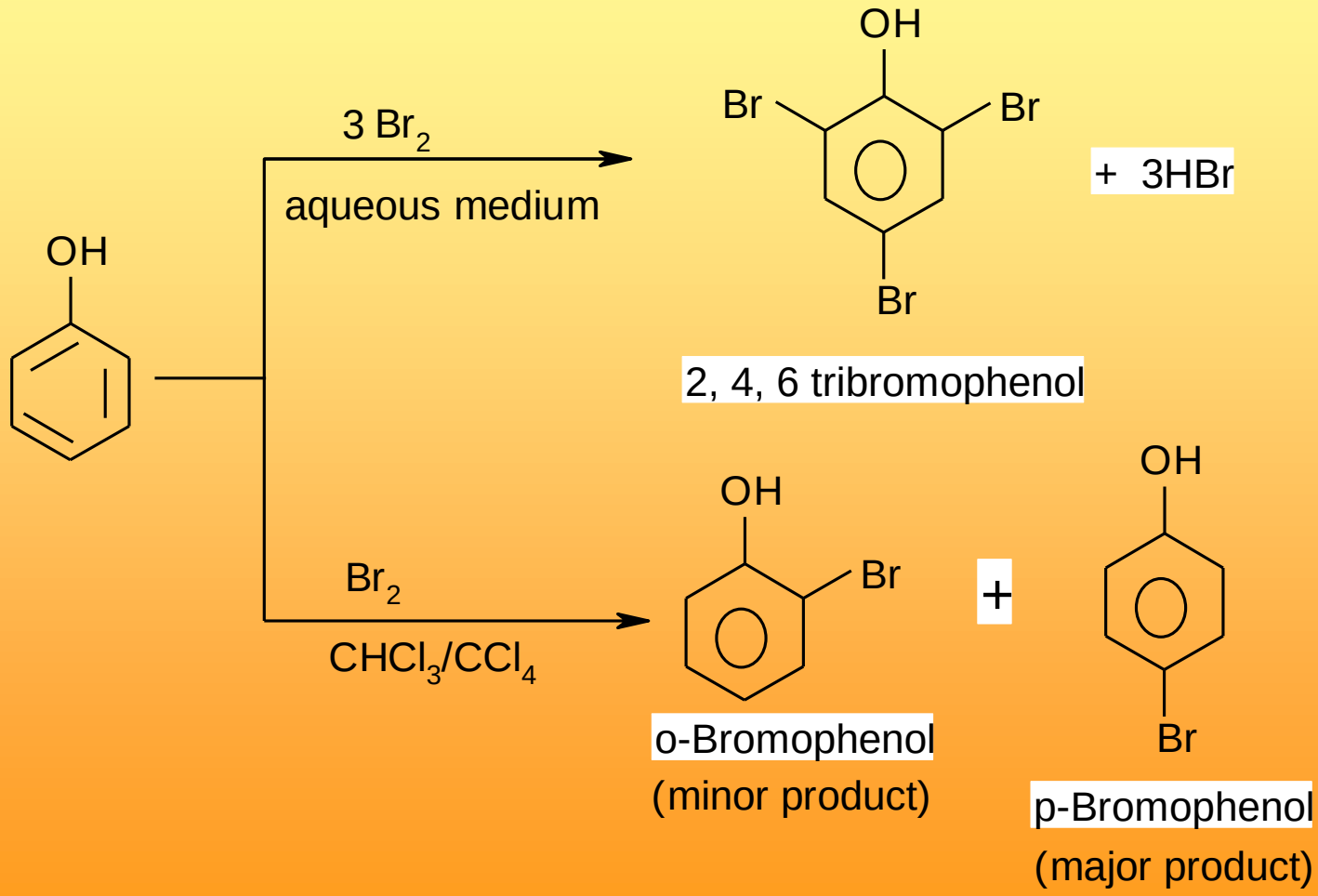
With dilute HNO_3, it gives ortho and para-isomers which can be separated easily by distillation.



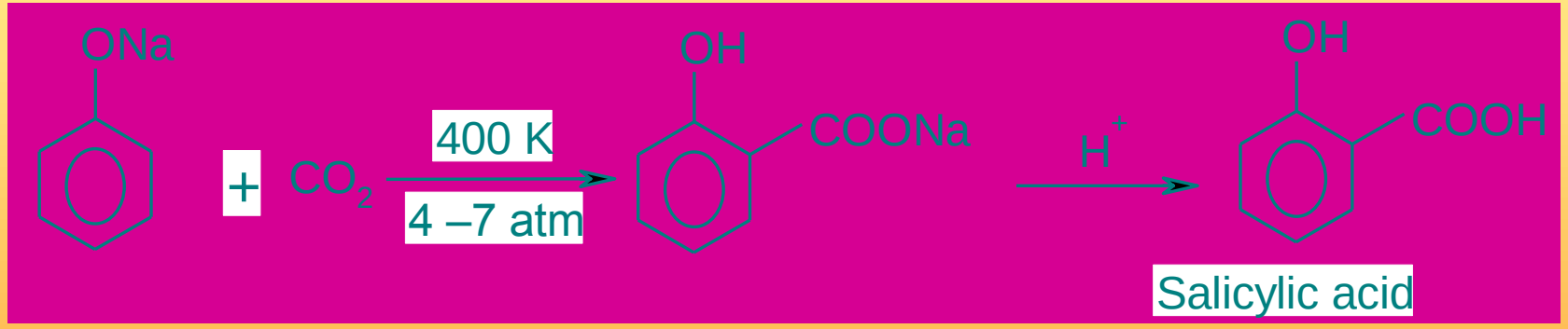
With concentrated HNO_3 phenol is converted to 2,4,6-trinitrophenol.



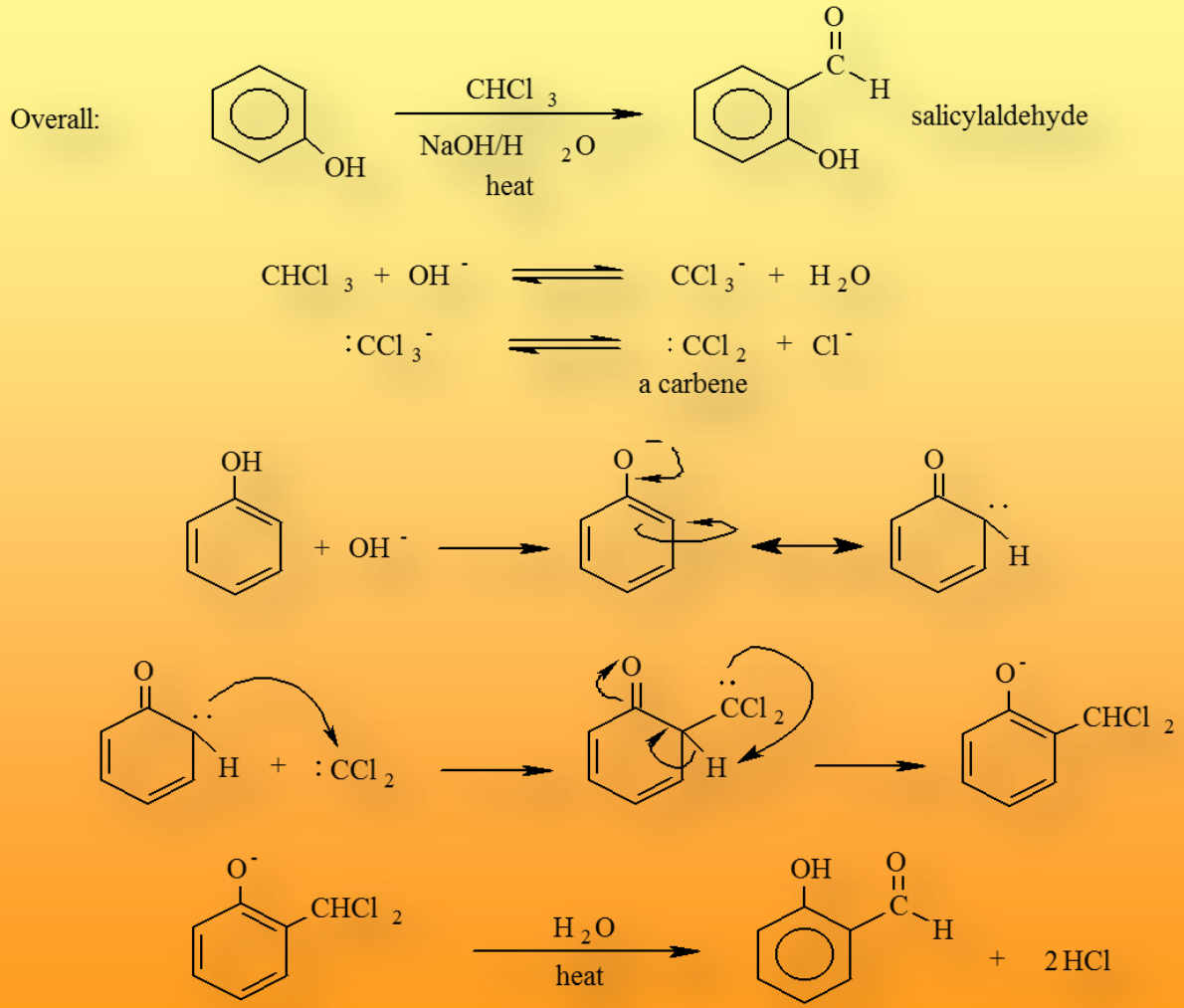
Bromination of phenol



Kolbe's reaction

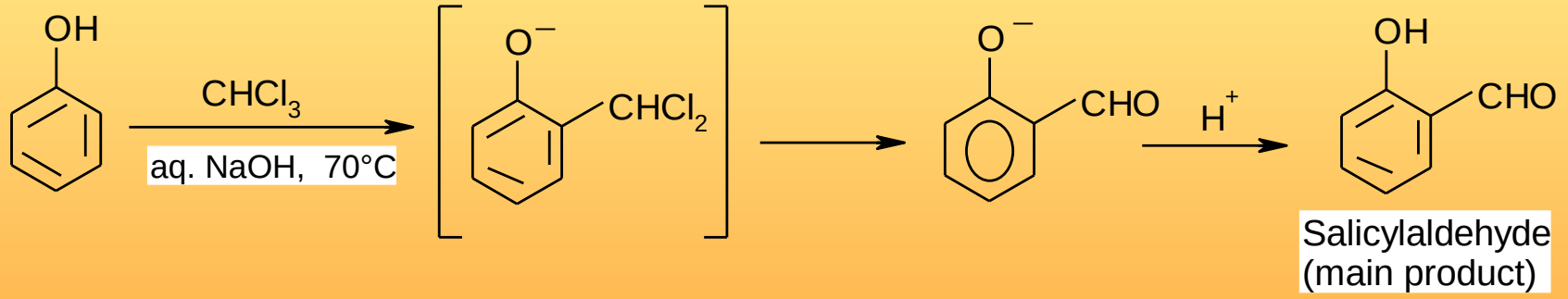


Reimer-Tiemann Reaction Mechanism



Reimer Tiemann Reaction

On treating phenol with chloroform in presence of sodium hydroxide, a —CHO group is introduced at ortho position of benzene ring.

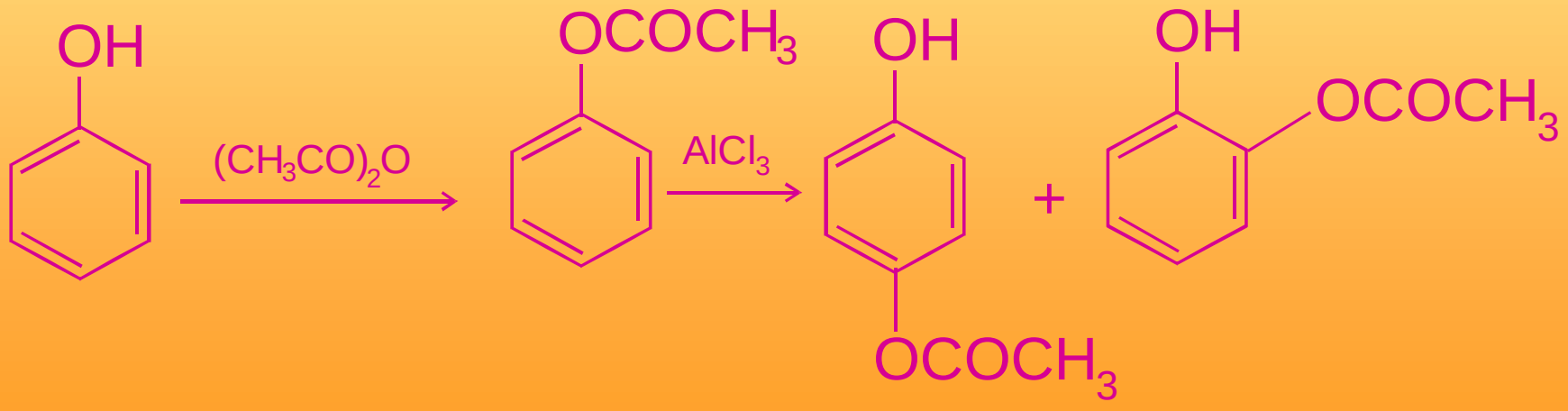


The mechanism involves dichlorocarbene as an intermediate

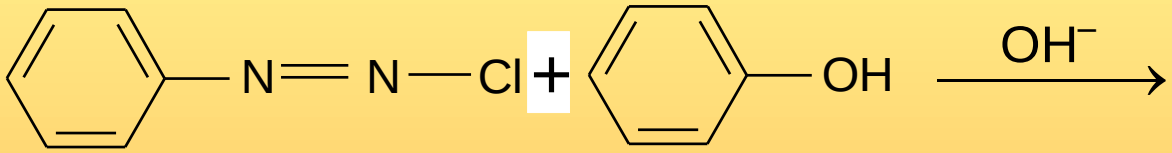
$$OH^- + CHCl_3 \; f \; H_2O + {}^-{:}CCl_3 \longrightarrow Cl^- + {:}CCl_2$$

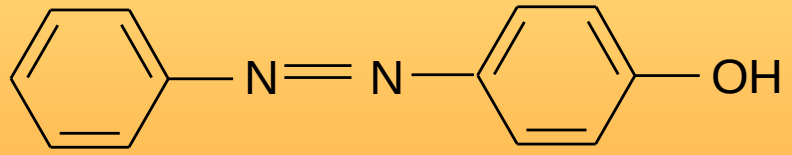
Fries rearrangement

Esters of phenols yield phenolic ketones on treatment with anhydrous aluminium chloride.



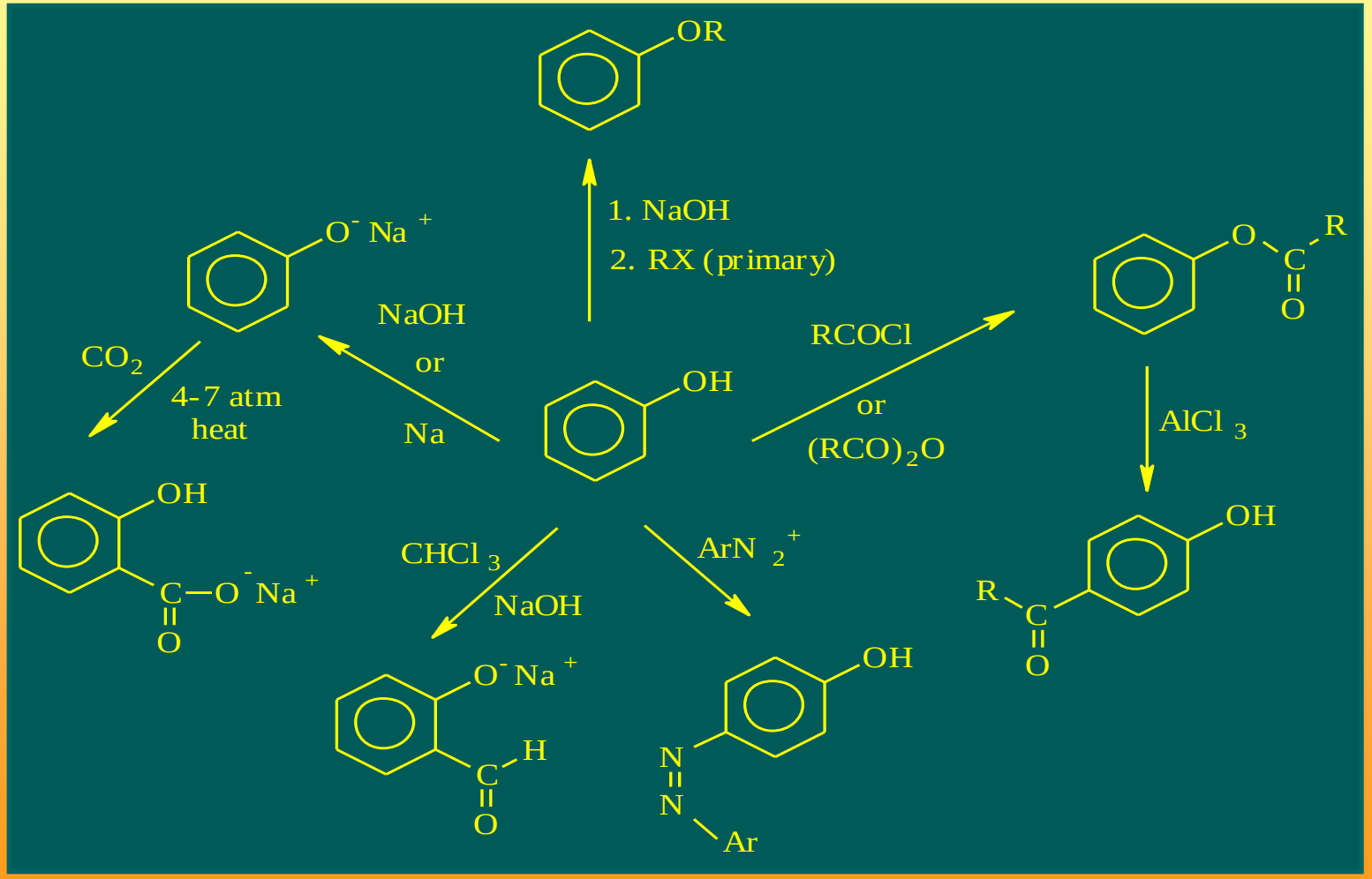
Coupling Reaction





p-hydroxy azo benzene

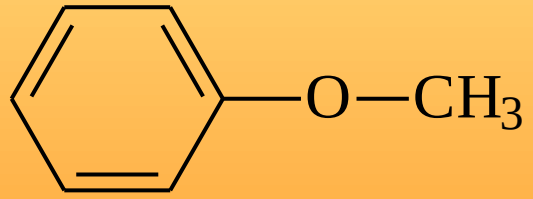
Phenol Reactions: A Summary

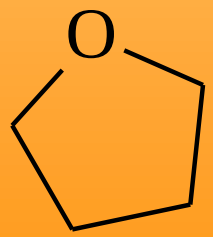


Ethers

Introduction

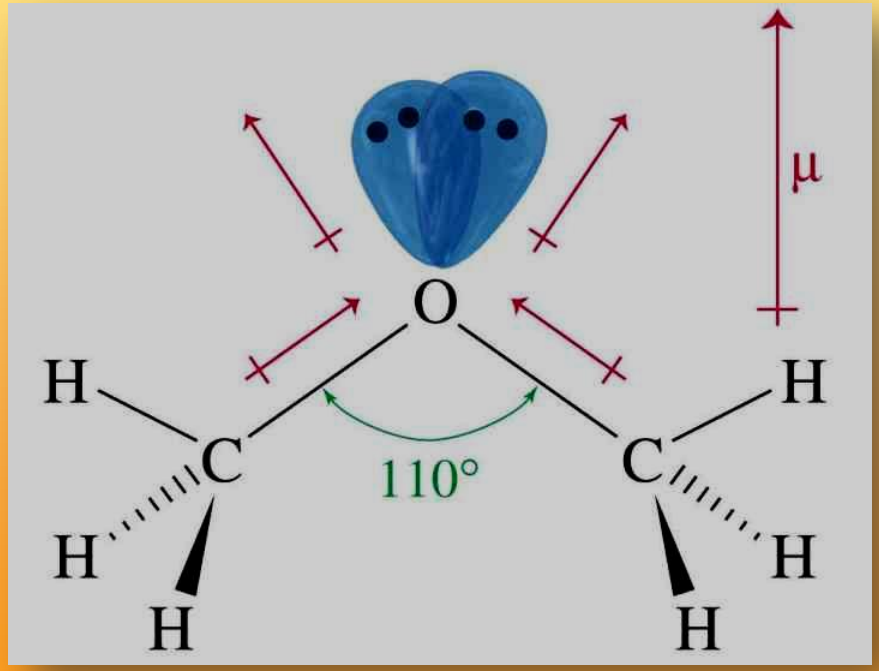
- **Formula R-O-R where R is alkyl or aryl.**
- **Symmetrical or unsymmetrical**
- **Examples:**

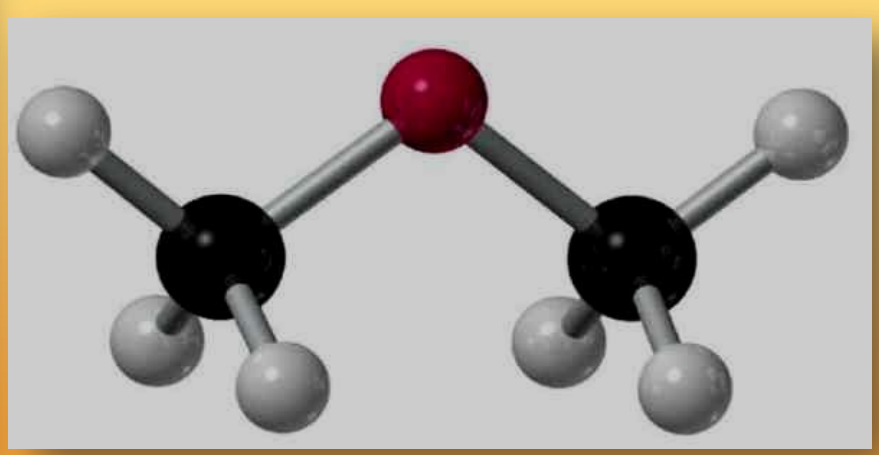




Structure and Polarity

- **Bent molecular geometry**
- **Oxygen is sp^3 hybridized**
- **Tetrahedral angle**

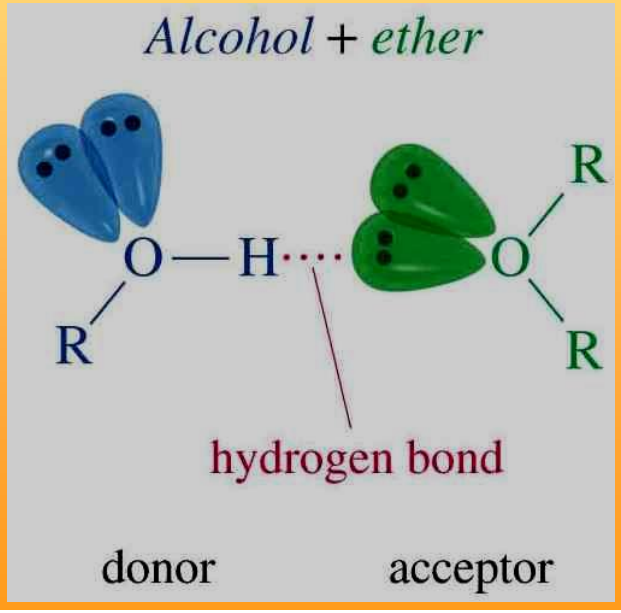




Hydrogen Bond Acceptor

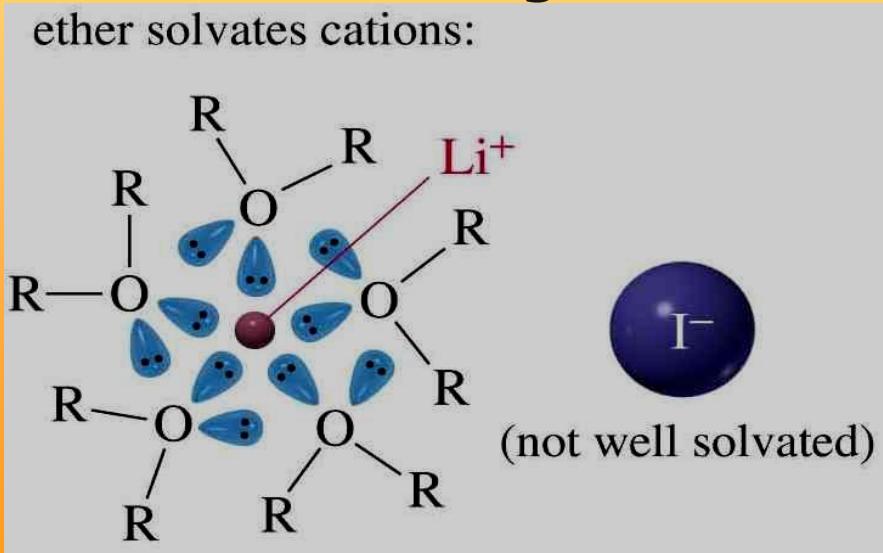
Ethers cannot H-bond to each other.

In the presence of -OH or -NH (donor), the lone pair of electrons from ether forms a hydrogen bond with the -OH or -NH.



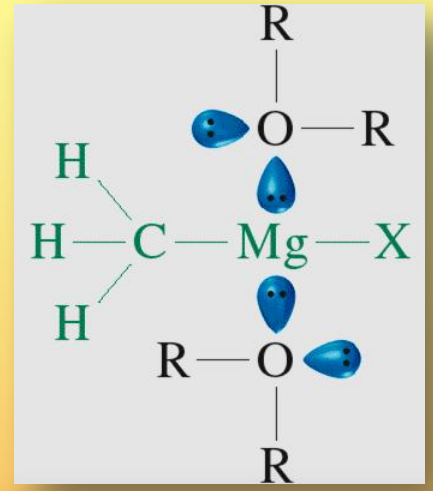
Solvent properties

- **Nonpolar solutes dissolve better in ether than in alcohol.**
- **Ether has large dipole moment, so polar solutes <u>also</u> dissolve.**
- **Ethers solvate cations.**
- **Ethers do not react with strong bases.**

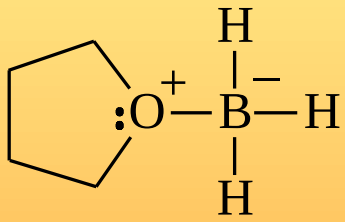


Ether complexes

- **Grignard reagents**

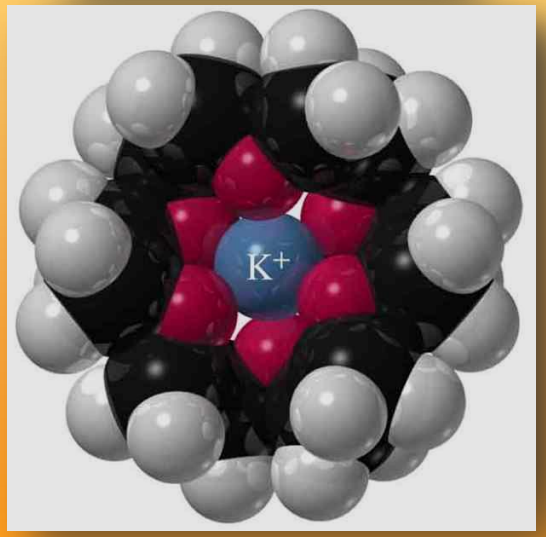


- **Electrophiles**



$BH_3 \cdot THF$

- **Crown ethers**

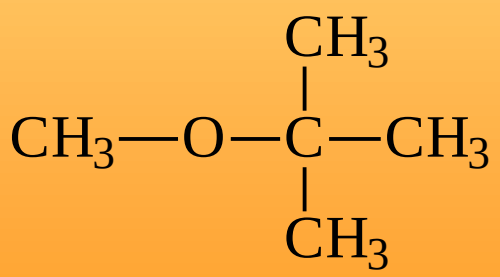


Nomenclature

Common name

- **Alkyl alkyl ether**
- **Current rule: alphabetical order**
- **Old rule: order of increasing complexity**
- **Symmetrical: use dialkyl, or just alkyl.**
- **Examples:**

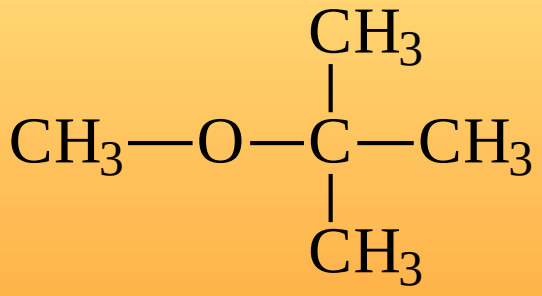
diethyl ether or ethyl ether



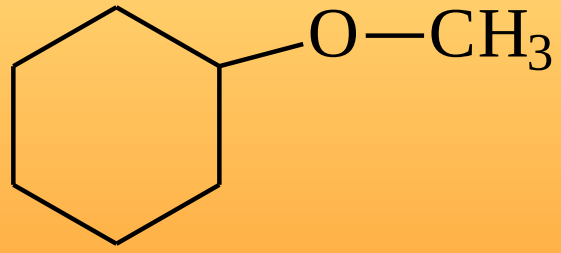
***t*-butyl methyl ether or methyl *t*-butyl ether =>**

IUPAC Names

- **Alkoxy alkane**
- **Examples:**



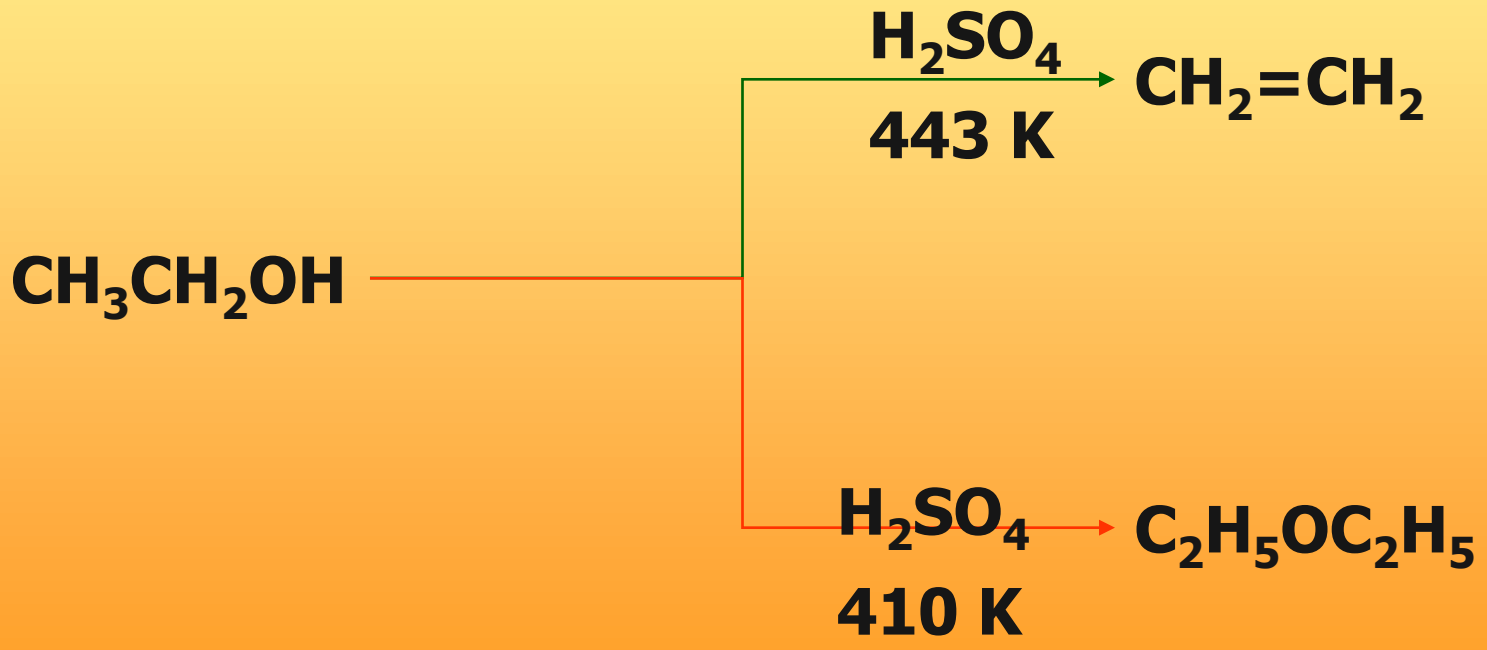
2-methyl-2-methoxypropane



Methoxycyclohexane

Preparation

By dehyration of alcohols



Williamson's Process

Important laboratory method for the preparation of symmetrical and unsymmetrical ethers.

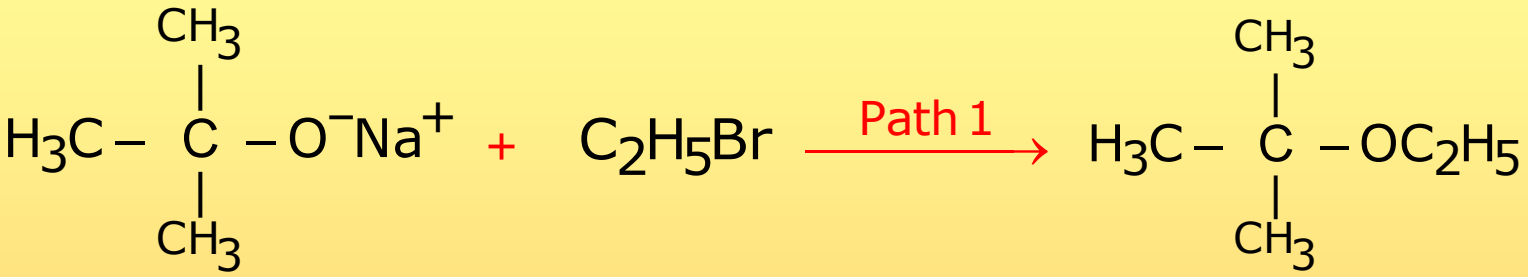
$$ROH + Na \longrightarrow RO^{-}Na^{+} + \frac{1}{2}H_2$$

$$RO^{-} + R`{-}X^{-} \xrightarrow{S_N2} R-O-R` + X^{-}$$

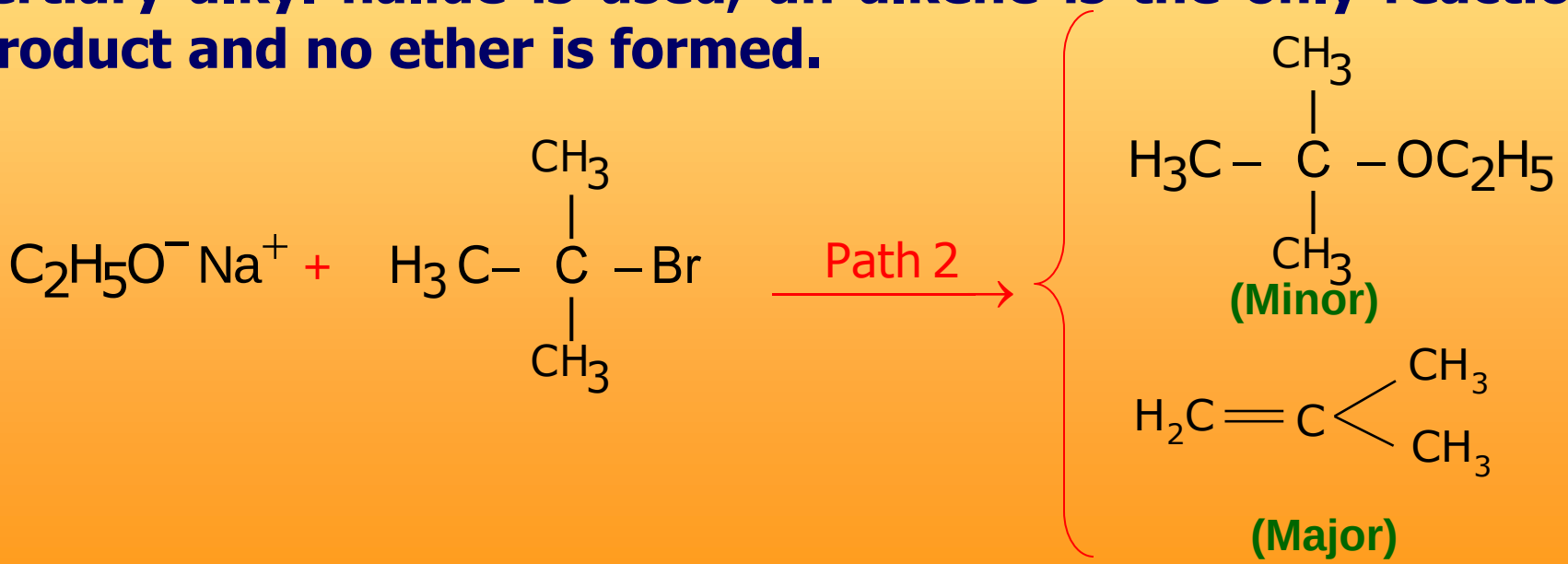
But R`X → Must be 1^0.

2^0 and 3^0 R`X → Alkene will be the major product

Williamsons Process



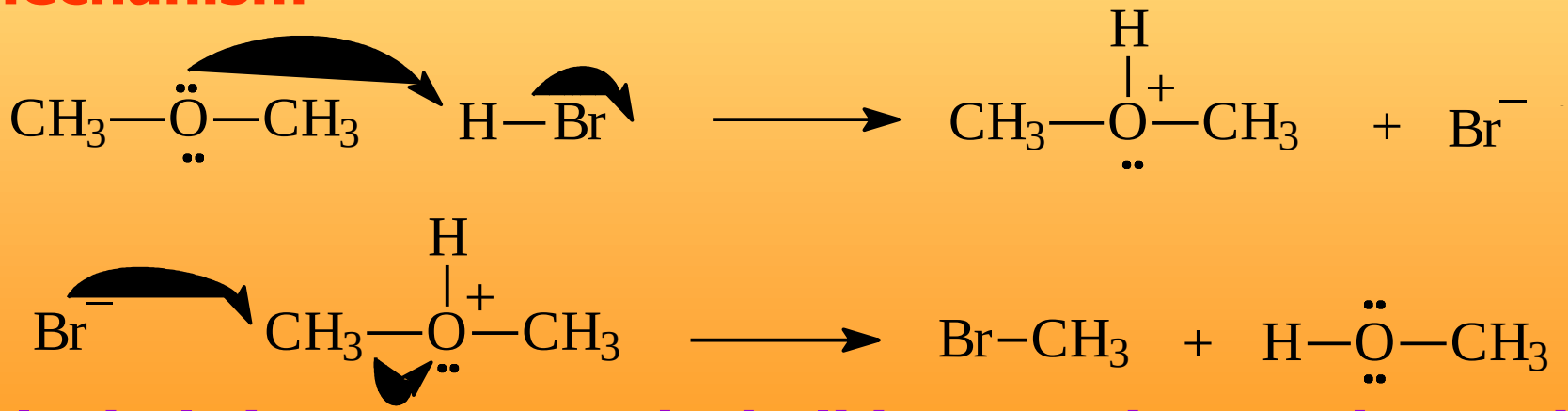
Best results are obtained if the alkyl halide is primary. If tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed.



Cleavage of Ethers

- **Ethers are unreactive toward base, but protonated ethers can undergo substitution reactions with strong acids.**
- **Alcohol leaving group is replaced by a halide.**
- **Reactivity: HI > HBr >> HCl**

Mechanism

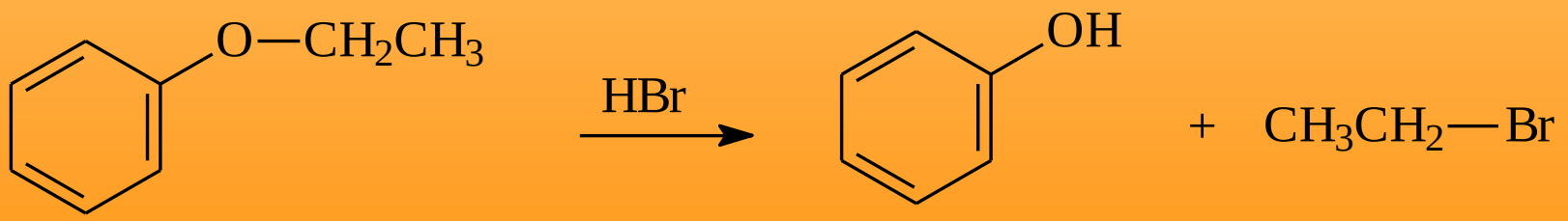


Alcohol is protonated, halide attacks, and another molecule of alkyl bromide is formed.

Phenyl Ether Cleavage

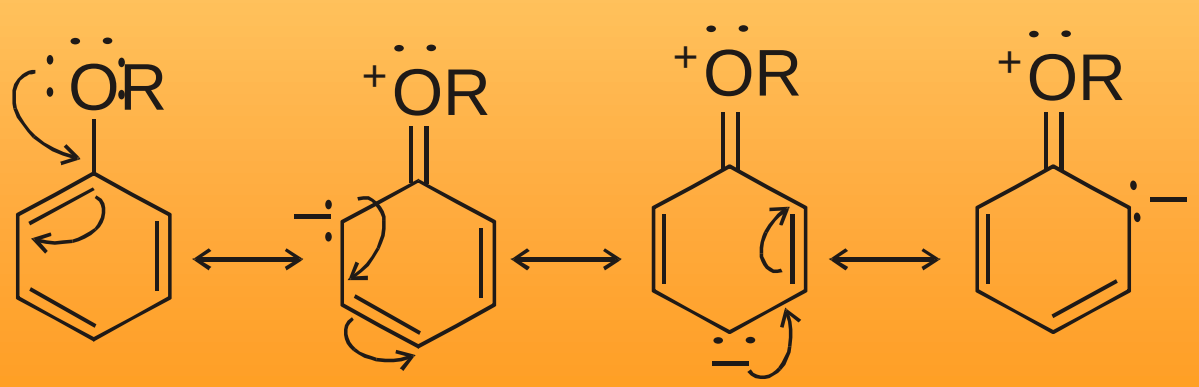
Alkyl aryl ethers are cleaved at the alkyl oxygen bond due to the low reactivity of aryl-oxygen bond.

- **Phenol cannot react further to become halide.**
- **Example:**



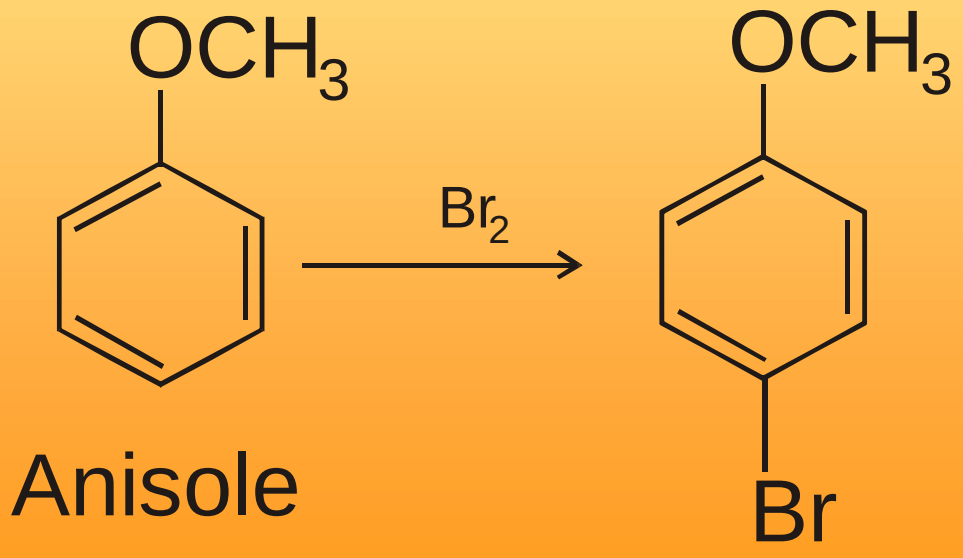
Electrophilic substitution in alkyl aryl ethers

The alkoxy group(-OR) is ortho, para directing and activate the aromatic ring towards electrophilic substitution in the same way as phenol.



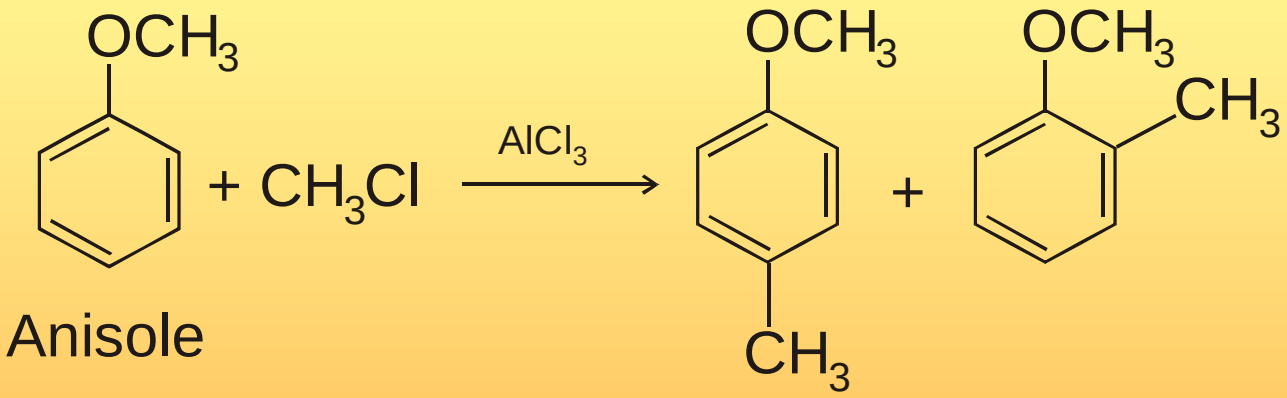
Helogenation

Anisole undergoes bromination with bromine in ethanoic acid even in absence of iron(III) bromide catalyst.



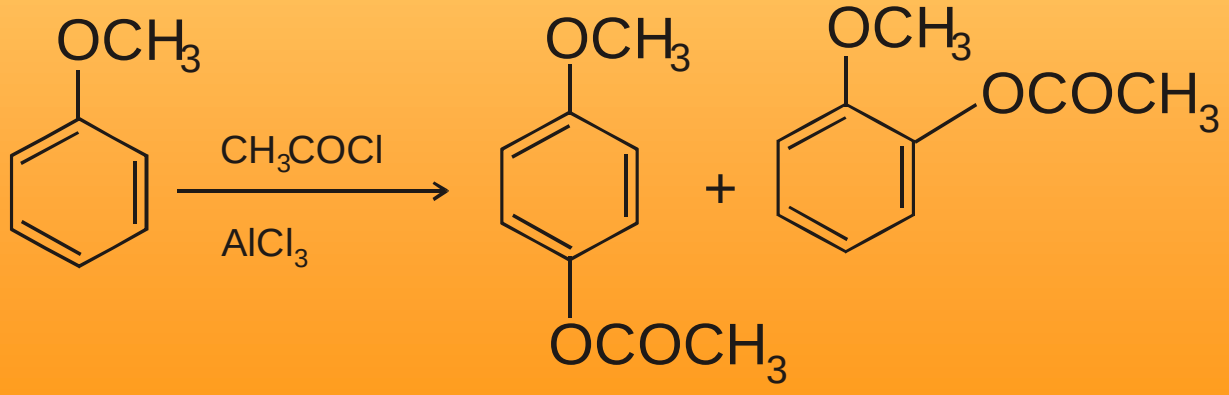
Friedel Craft reaction

Alkylation



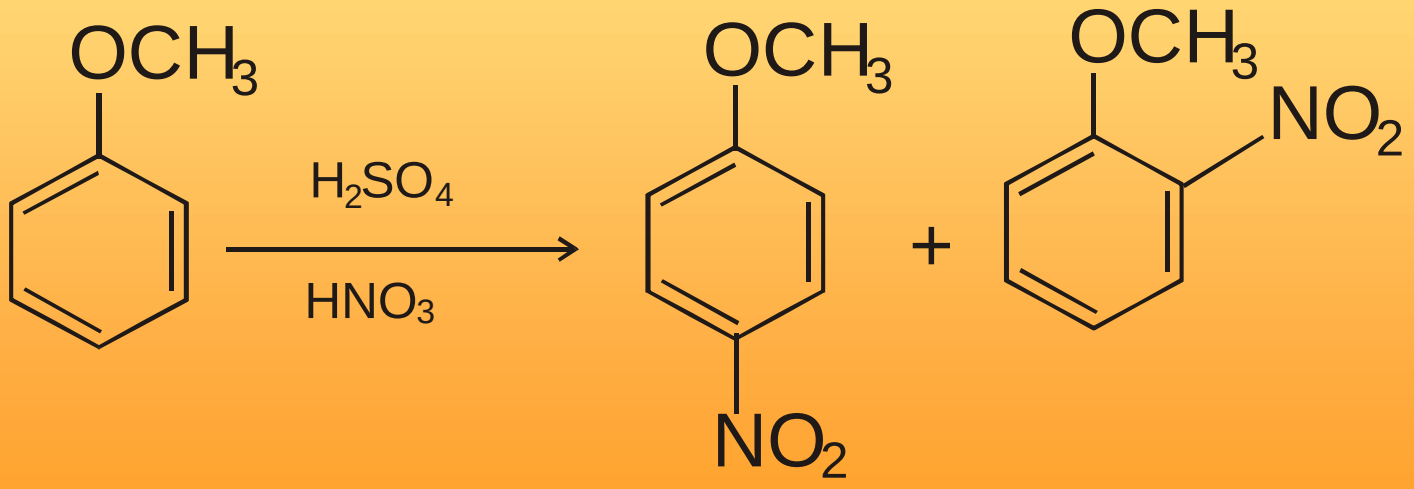
Anisole

Acylation



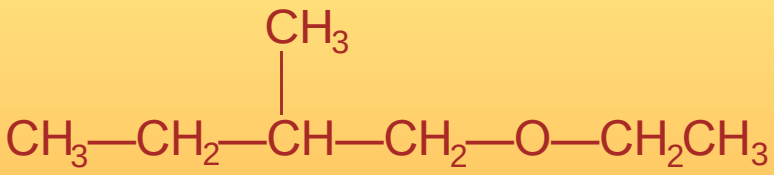
Nitration

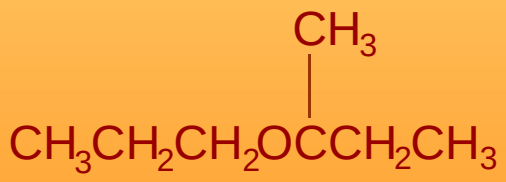
Obtained mixture of ortho and para isomers.



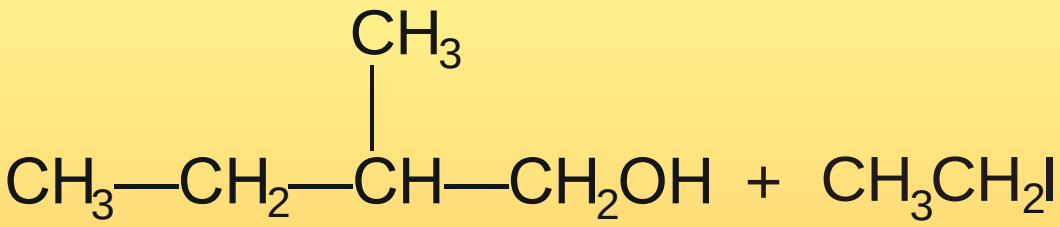
Illustrative Example

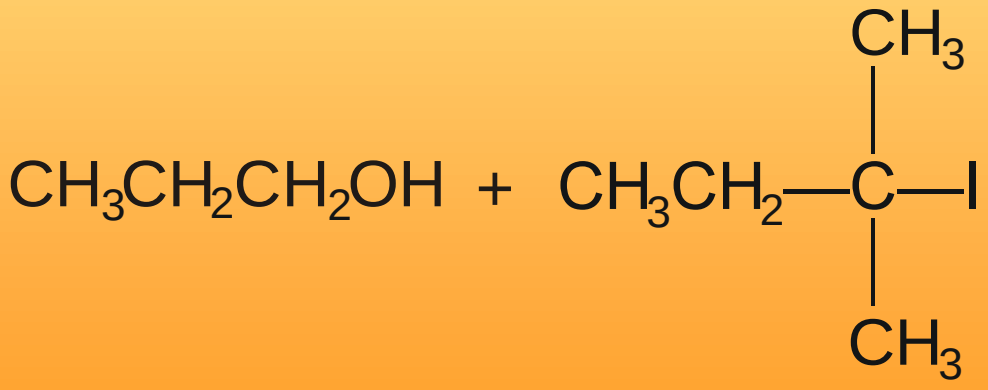
Give the major products that are formed by heating each of the following ethers with HI.

(i) 

(ii) 

Solution

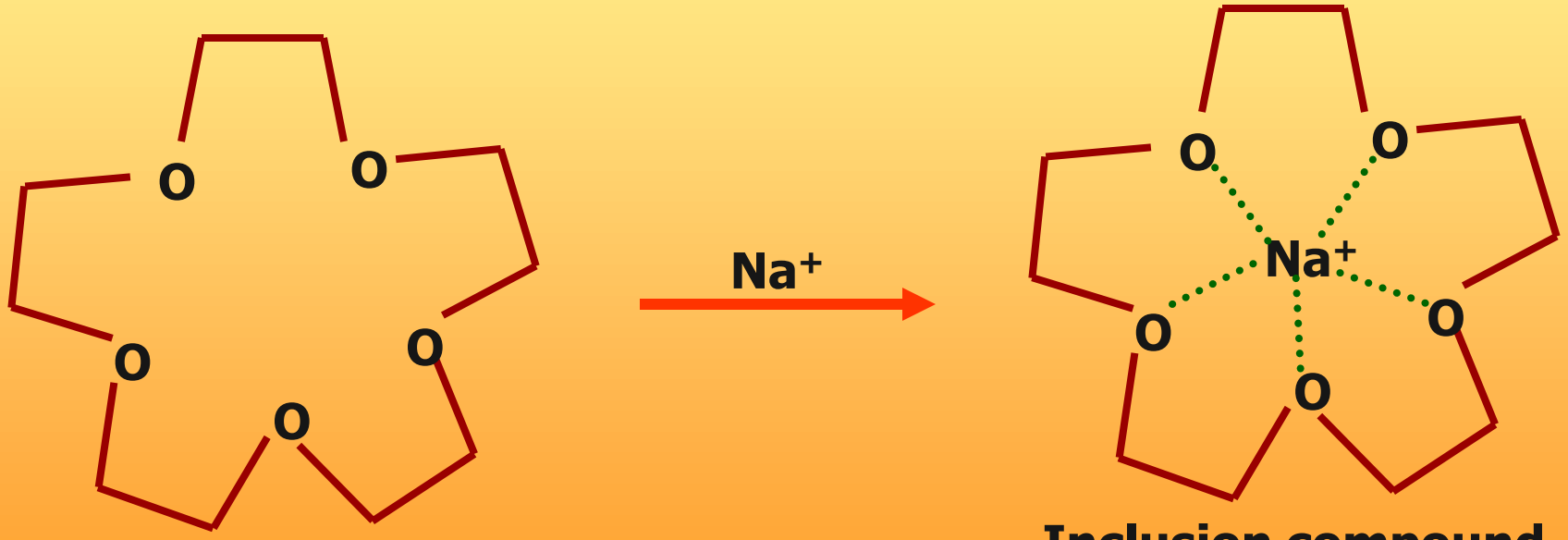
(i) 

(ii) 

Crown ethers

Cyclic polyethers containing four or more ether linkages in a ring of twelve or more atoms.

Crown ethers bind certain metal ions depending on size of the cavity



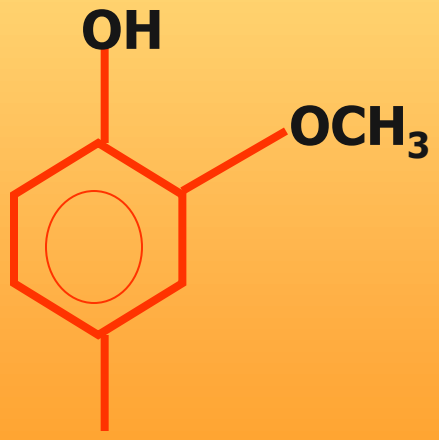
Inclusion compound

In this reaction crown ether is host and metal ion is guest.
Crown ethers allow inorganic salts to dissolve in non-polar solvents.

Uses of ethers

As solvent and inhalation anaesthetic.

A number of naturally occurring phenol and ethers are used as flavourings and in perfumes of their pleasant odour.



Vanillin

Thanks…