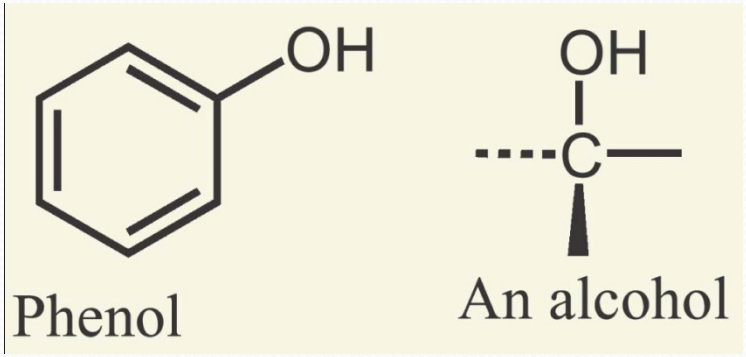
ALCOHOLS, PHENOLS & ETHERS

ALCOHOLS & PHENOLS

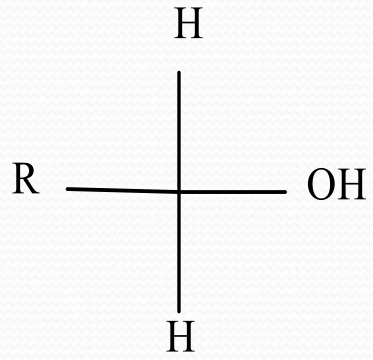
- Alcohols contain an OH group connected to a a saturated C (sp^3).
- They are important solvents and synthesis intermediates.
- Phenols contain an OH group connected to a carbon in a benzene ring.
- Methanol, CH_3OH, called methyl alcohol, is a common solvent, a fuel additive, produced in large quantities.
- Ethanol, CH_3CH_2OH, called ethyl alcohol, is a solvent, fuel, beverage.
- Phenol, C_6H_5OH ("phenyl alcohol") has diverse uses - it gives its name to the general class of compounds.



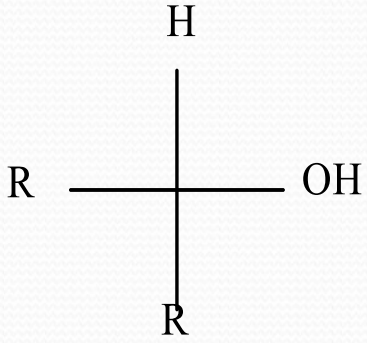
ALCOHOLS

Naming Alcohols:

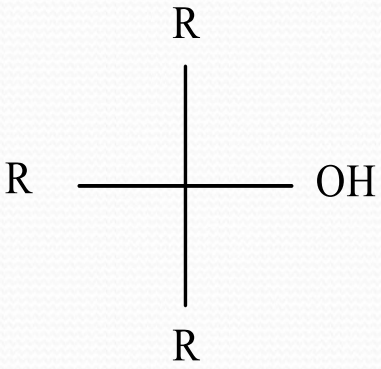
Alcohols are classified as primary (1˚), secondary (2˚) or tertiary (3) alcohols



Primary Alcohols



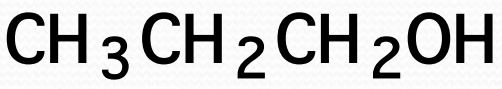
Secondary Alcohols



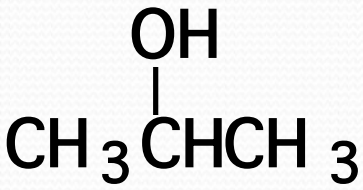
Tertiary Alcohols

IUPAC Rules for Naming Alcohols

- Select the longest carbon chain containing the hydroxyl group, and derive the parent name by replacing the -*e* ending of the corresponding alkane with -*ol* .
- Number the chain from the end nearer the hydroxyl group.
- Number substituents according to position on chain, listing the substituents in alphabetical order .



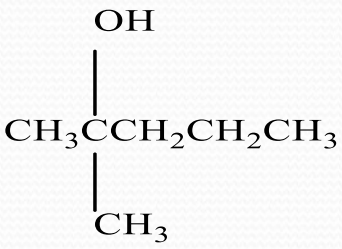
1-Propanol
(Propyl alcohol)



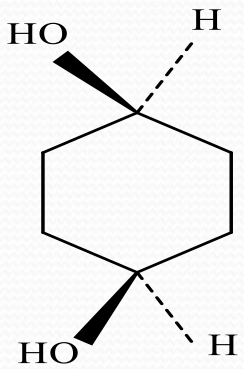
2-Propanol
(Isopropyl alcohol)

1-Butanol
(Butyl alcohol)

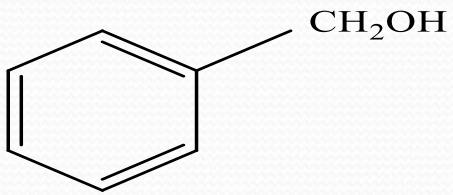
EXAMPLES



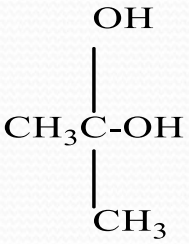
2-Methylpentan-2-ol



cic-Cyclohexane-1,4-diol

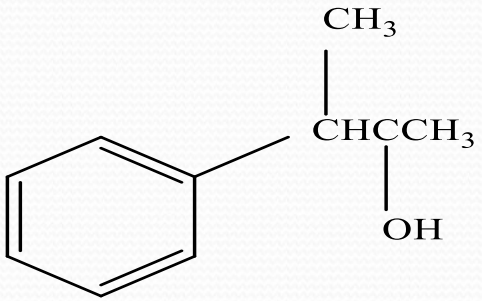


Benzyl alcohol



tert-Butyl alcohol

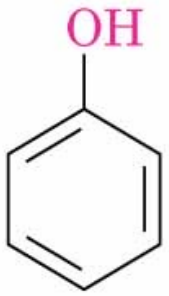
Ethane-1,2-diol



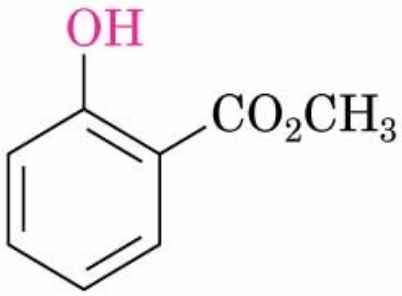
3-Phenylbutan-2-ol

NAMING PHENOLS

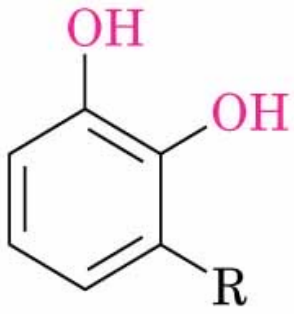
- Use “phene” (the French name for benzene) as the parent hydrocarbon name, not benzene.
- Name substituents on aromatic ring by their position from OH.



Phenol (also known as carbolic acid)



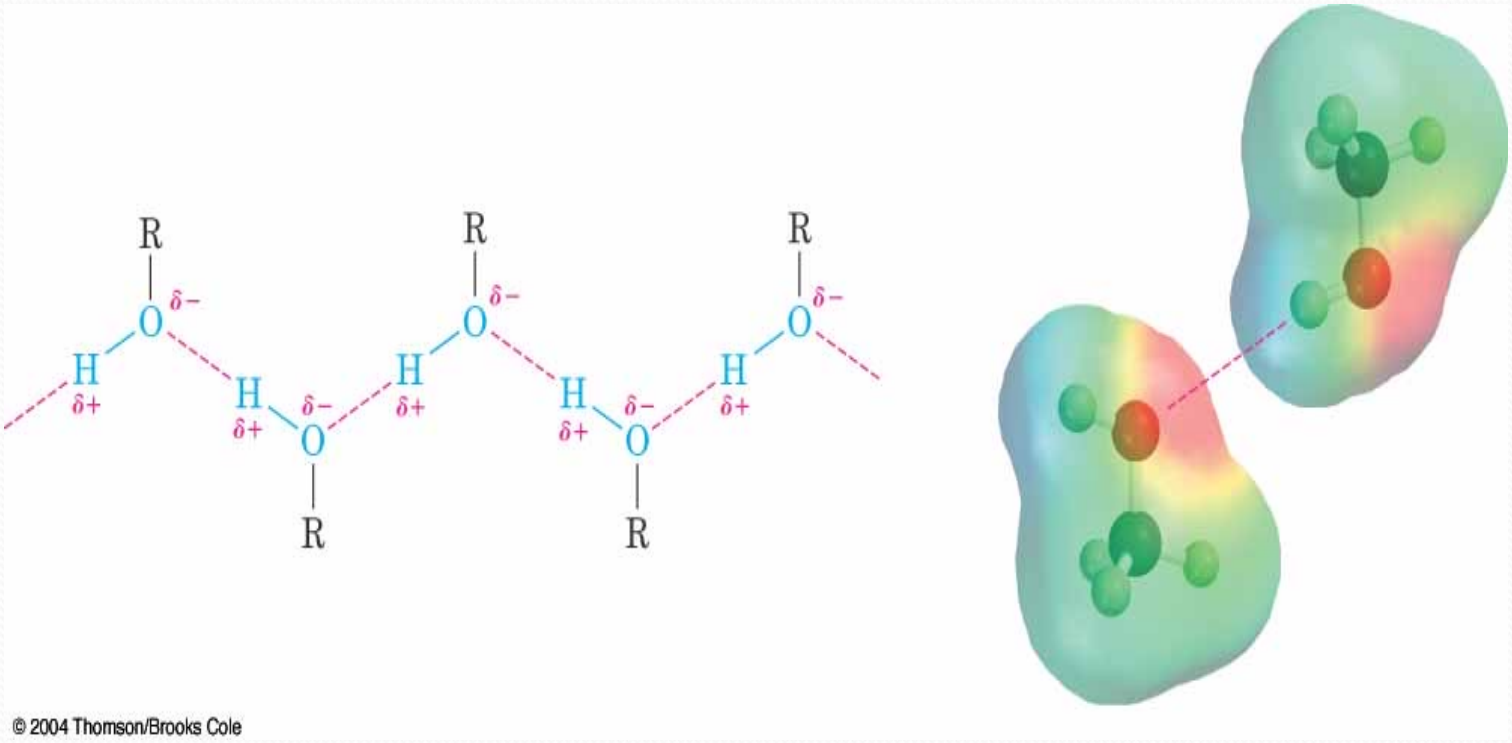
Methyl salicylate



Urushiols (R = different C_{15} alkyl and alkenyl chains)

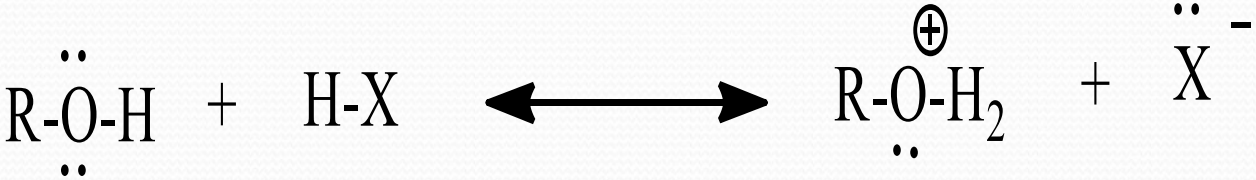
Properties Of Alcohols And Phenols

- Alcohols are polar compounds.
- Alcohols and phenols have high boiling points, as they can form hydrogen bonds in liquid state.

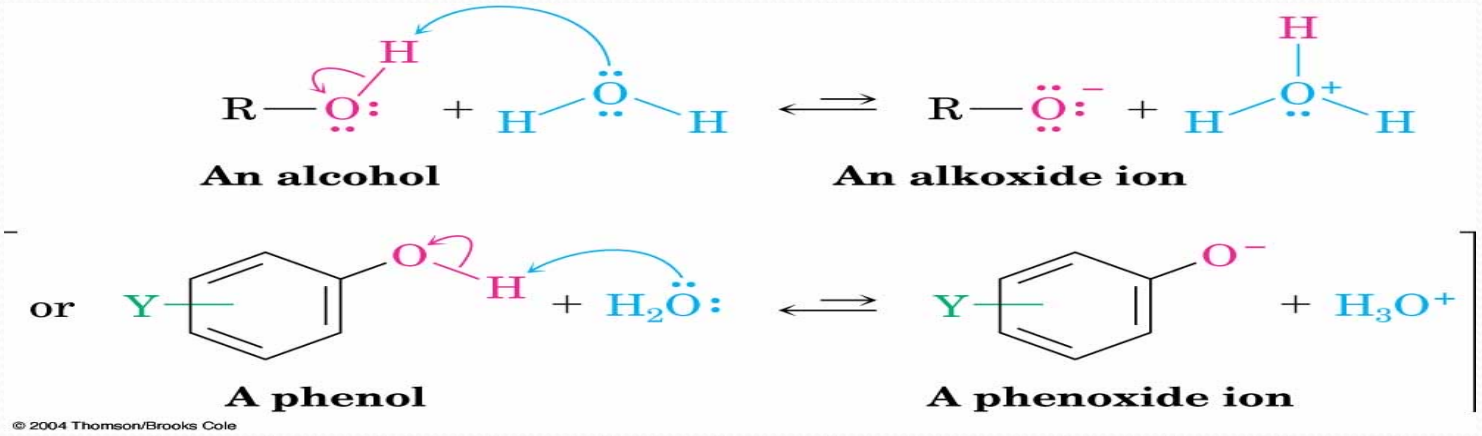


ACIDITY OF ALCOHOLS AND PHENOLS

- Alcohols and phenols, like water, are both weakly basic and weakly acidic.
- As Lewis bases, alcohols and phenols are reversibly protonated by strong acids to form oxonium ions (ROH_2).

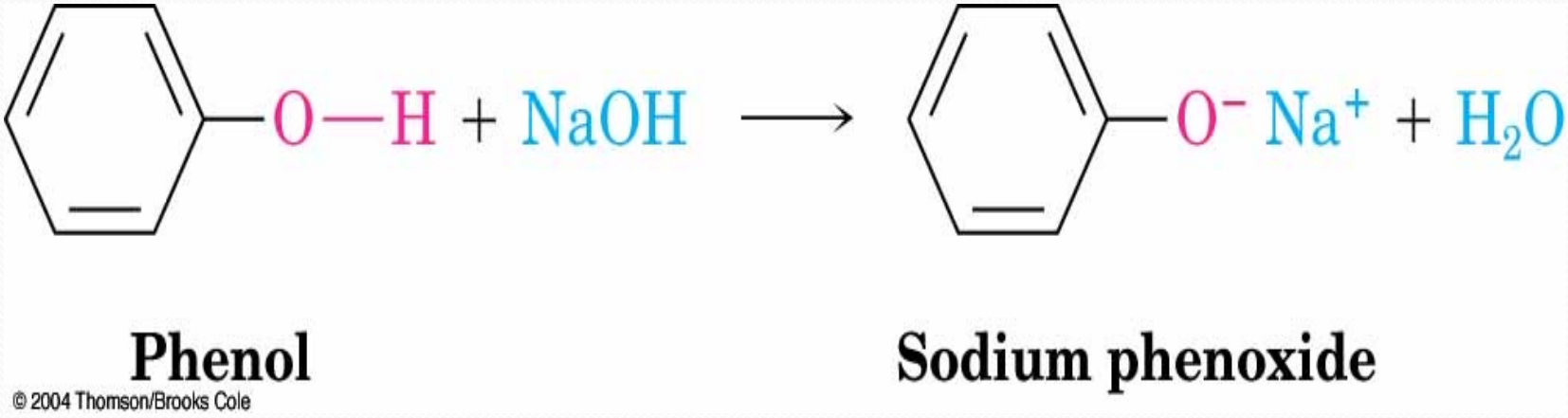


- As weak acids, alcohols and phenols dissociate to a slight extent in dilute aqueous solutions to form alkoxide ion or phenoxide ion.



Acidity Of Alcohols And Phenols

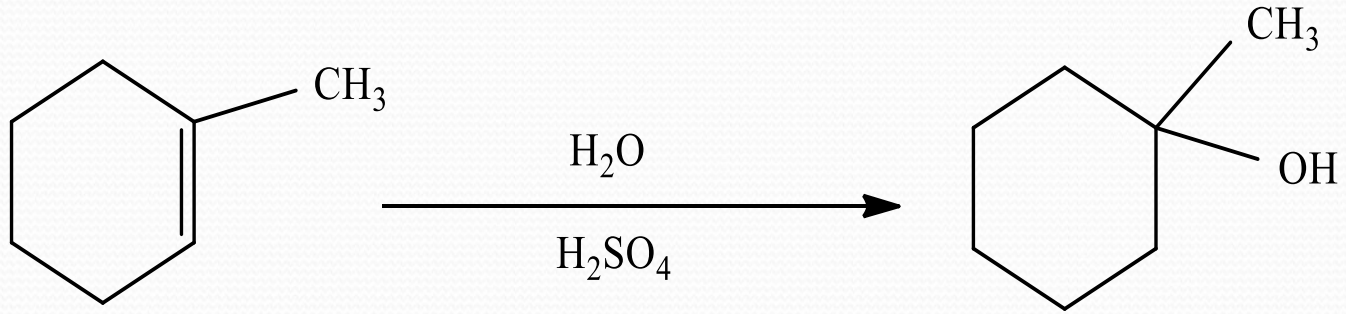
- Phenols are more acidic than alcohols, because the phenoxide anion is resonance-stabliised by the aromatic ring.
- Phenols react with NaOH solutions (but alcohols do not), forming soluble salts that are soluble in dilute aqueous.



Preparation Of Alcohols

1. Alcohols can be synthesized by hydration of alkenes:

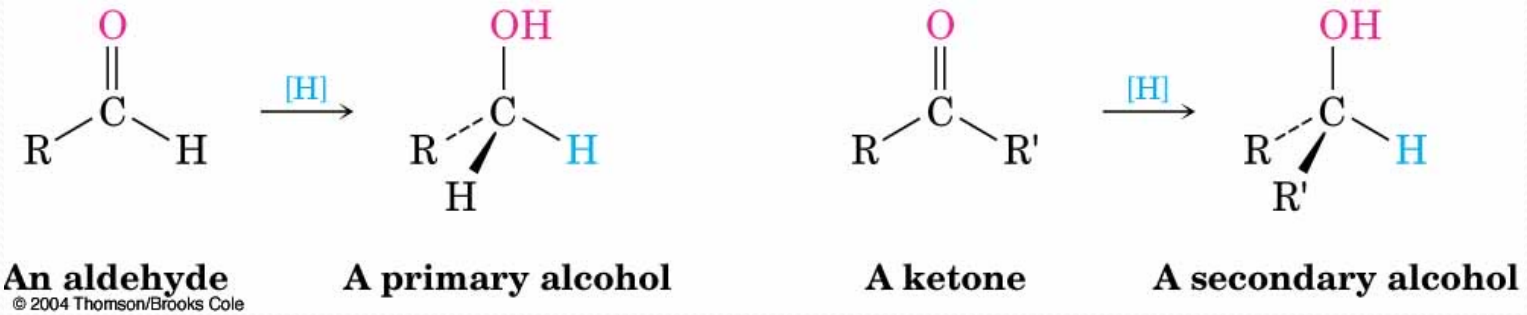
   Alkenes react with water in presence of H_2SO_4 as catalyst, leading towards a Markovnikov's product.



2. Reduction of Aldehydes and Ketones:

   Reduction of aldehydes yields primary alcohol.

   Reduction of ketones yield secondary alcohol.

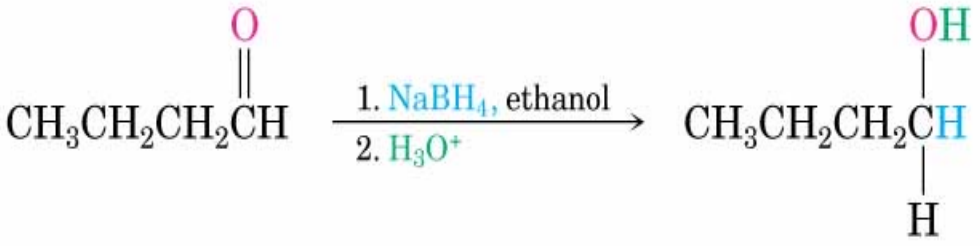


An aldehyde A primary alcohol A ketone A secondary alcohol

Preparation Of Alcohols

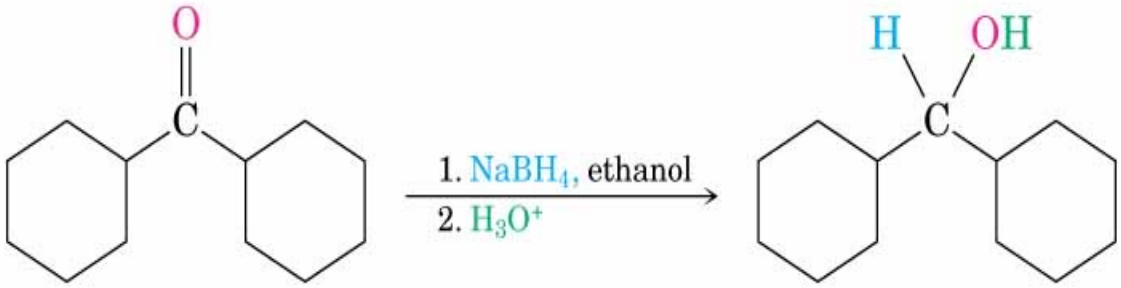
- In the reduction of aldehydes and ketones , sodium borohydride ($NaBH_4$) is used as a catalyst.

Aldehyde reduction



Butanal — **1-Butanol (85%) (a 1° alcohol)**

Ketone reduction

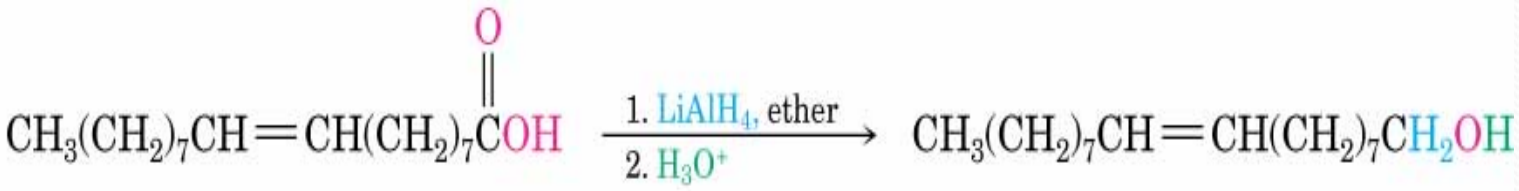


Dicyclohexyl ketone — **Dicyclohexylmethanol (88%) (a 2° alcohol)**

Preparation Of Alcohols

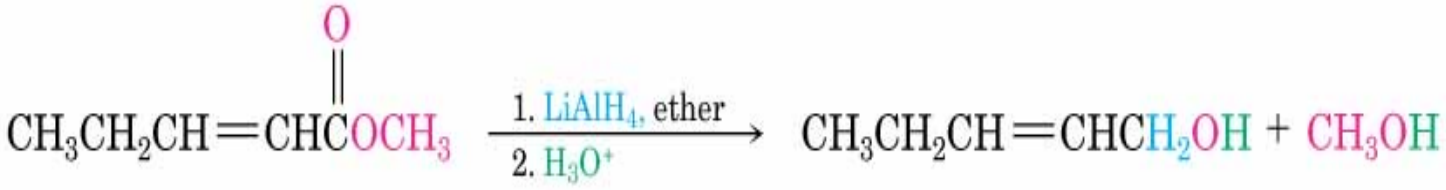
- Reduction of carboxylic acids and esters give primary alcohols.
- Lithium aluminium hydride ($LiAlH_4$) is used as a reducing agents, as it is a strong reducing agent.

Carboxylic acid reduction



9-Octadecenoic acid (Oleic acid) → **9-Octadecen-1-ol (87%)**

Ester reduction

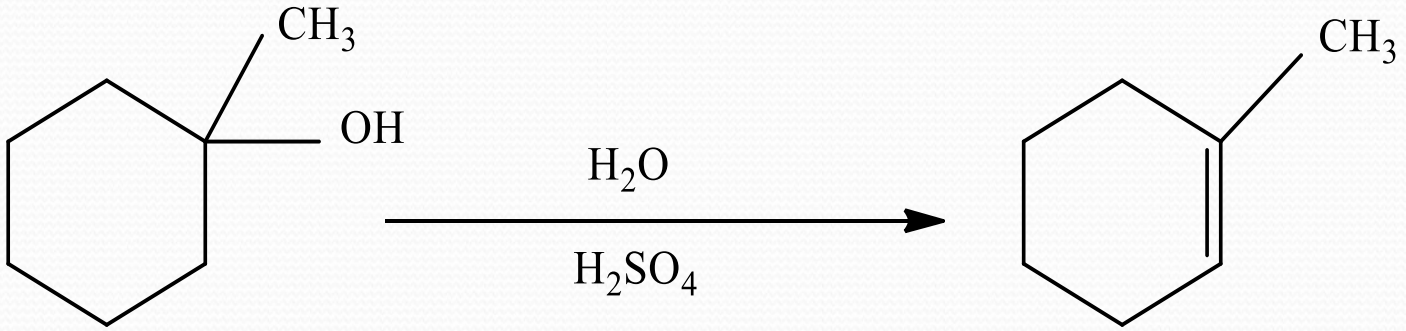


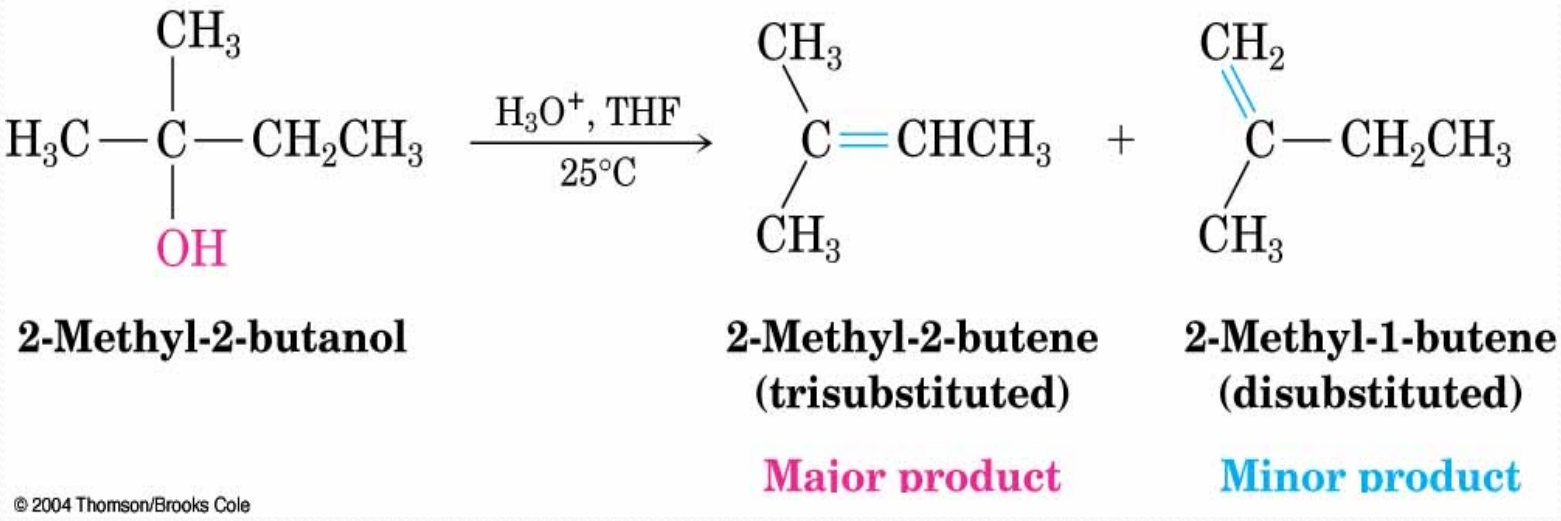
Methyl 2-pentenoate → **2-Penten-1-ol (91%)**

Reactions Of Alcohols

- Dehydration of alcohols:

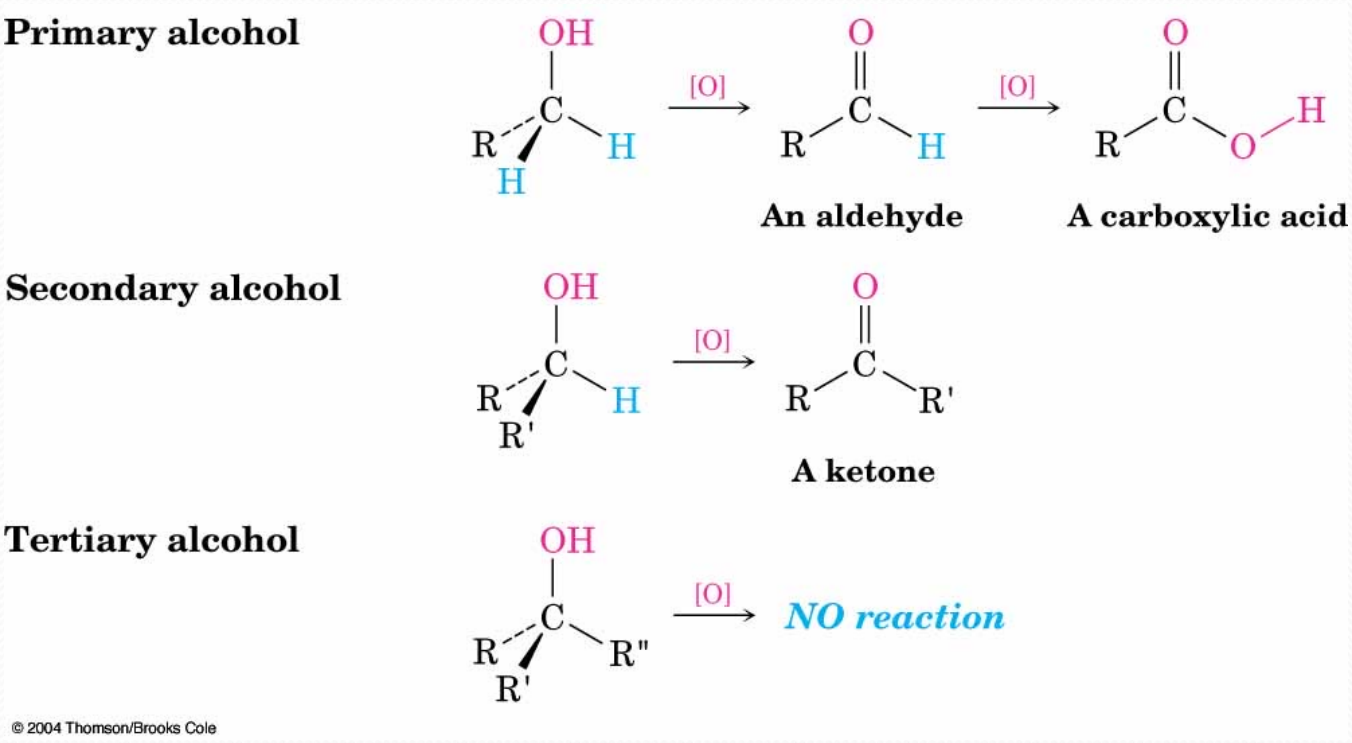
  Alcohols undergo dehydration with elimination of water to give alkenes.





Reactions of Alcohols

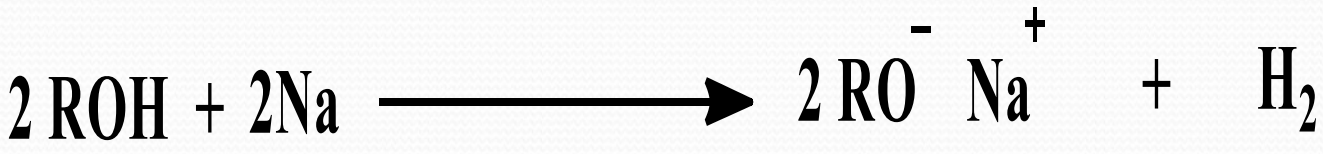
- Oxidation of alcohols:
- Primary alcohols yield aldehydes and carboxylic acids.
- Secondary alcohols yield ketones.
- Tertiary alcohols do not react with oxidizing agents.
- Oxidizing reagents , such as $KMnO_4$, CrO_3, and $Na_2Cr_2O_7$.

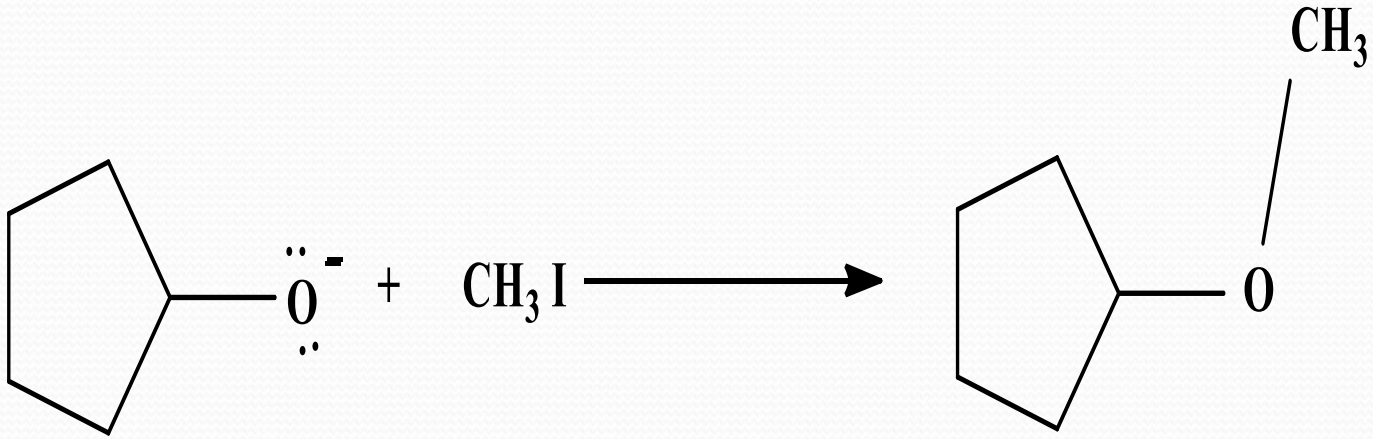


Reaction of Alcohols

- Williamson's ether synthesis:

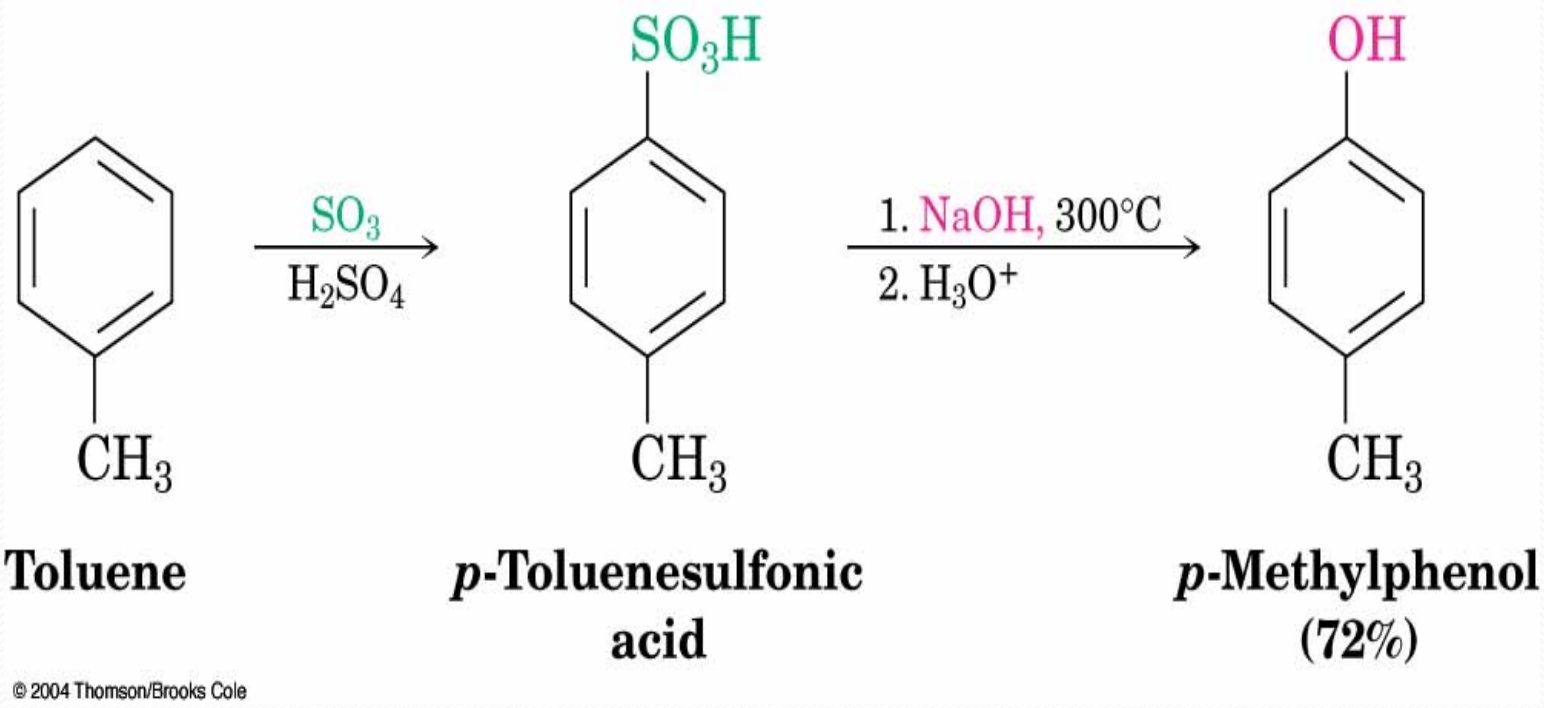
Alcohols react with sodium or potassium metal to form ethers.





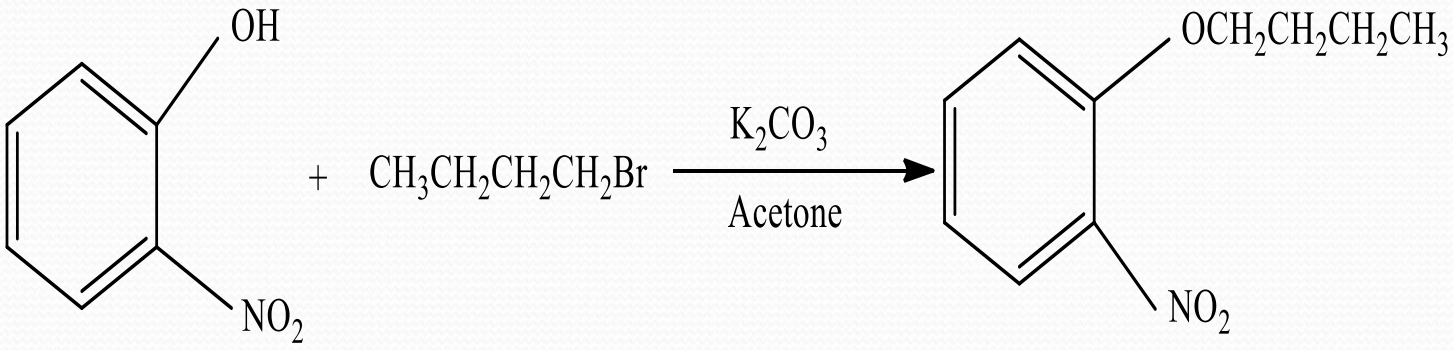
Preparation Of Phenols

- From aromatic sulfonic acids by melting with NaOH at high temperature.



Reactions Of Phenols

1. Phenols react with alkyl halides in presence of base to form ethers.

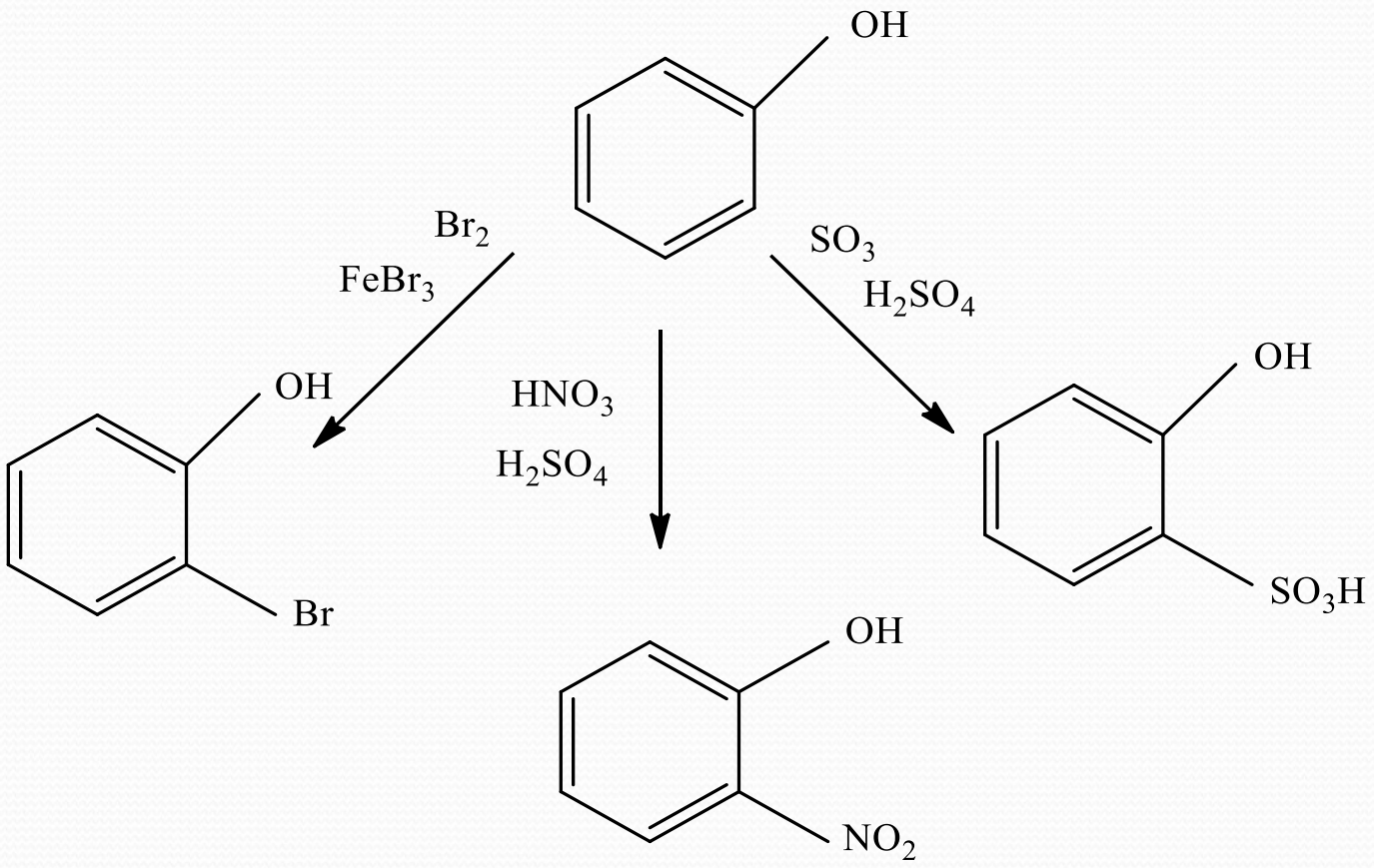


o-nitrophenol

Butyl-o-nitrophenyl ether

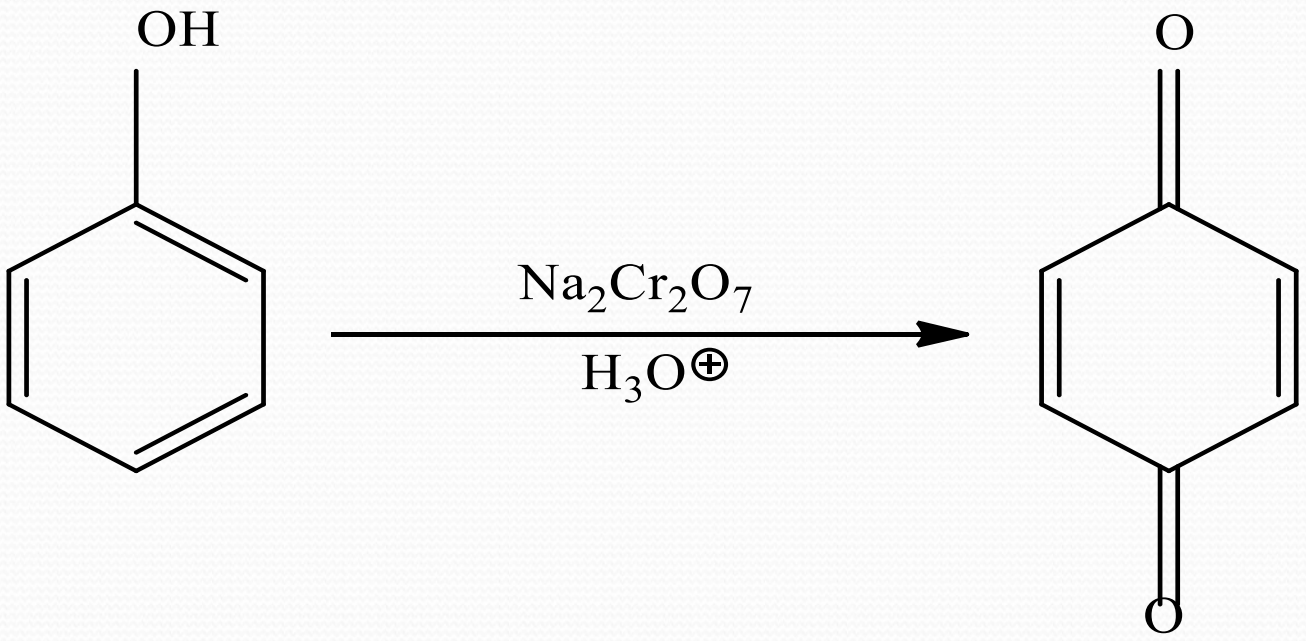
Electrophilic Aromatic substitution Reactions of Phenol

- The –OH group in phenol is *ortho*- and *para*- directing group.



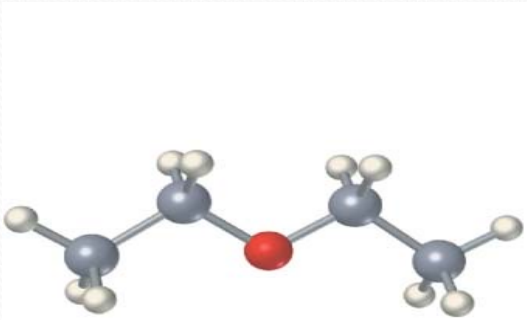
Reactions Of Phenols

- Phenols with strong oxidizing agents like, $Na_2Cr_2O_4$, yield quinones or cyclohexadienedione.



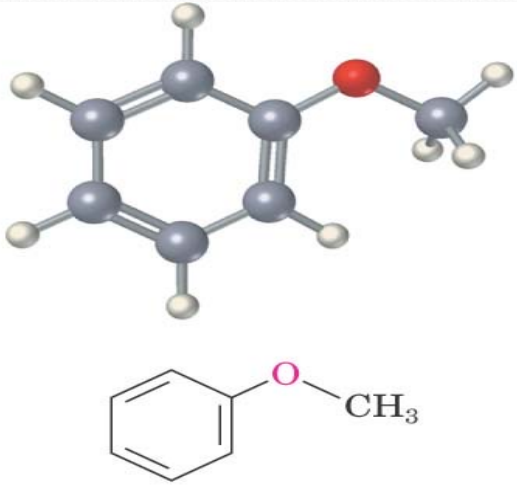
ETHERS

- Ethers have a functional group R-O-R.
- Example: CH_3OCH_3 Dimethyl ether.
- An ether has two organic groups (alkyl, aryl, or vinyl) bonded to the same oxygen atom, R–O–R′.
- Diethyl ether is used industrially as a solvent.
- Tetrahydrofuran (THF) is a solvent that is a cyclic ether.

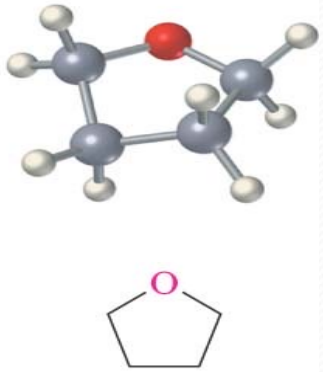


$CH_3CH_2—O—CH_2CH_3$

Diethyl ether



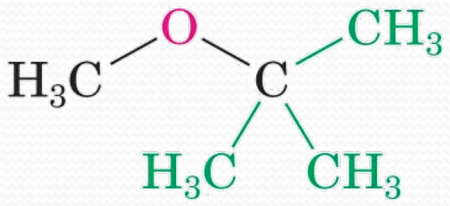
Anisole
(Methyl phenyl ether)



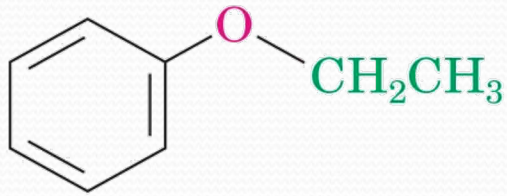
Tetrahydrofuran
(a cyclic ether)

Naming Ethers

- Simple ethers are named by identifying the two organic substituents and adding the word ether.
- If other functional groups are present, the ether part is considered an alkoxy substituent.

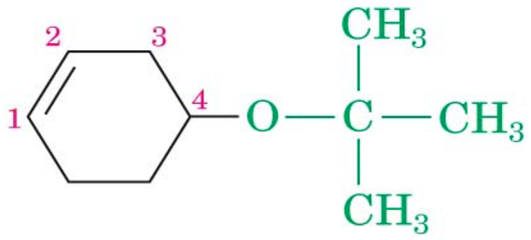


***tert*-Butyl methyl ether**



Ethyl phenyl ether

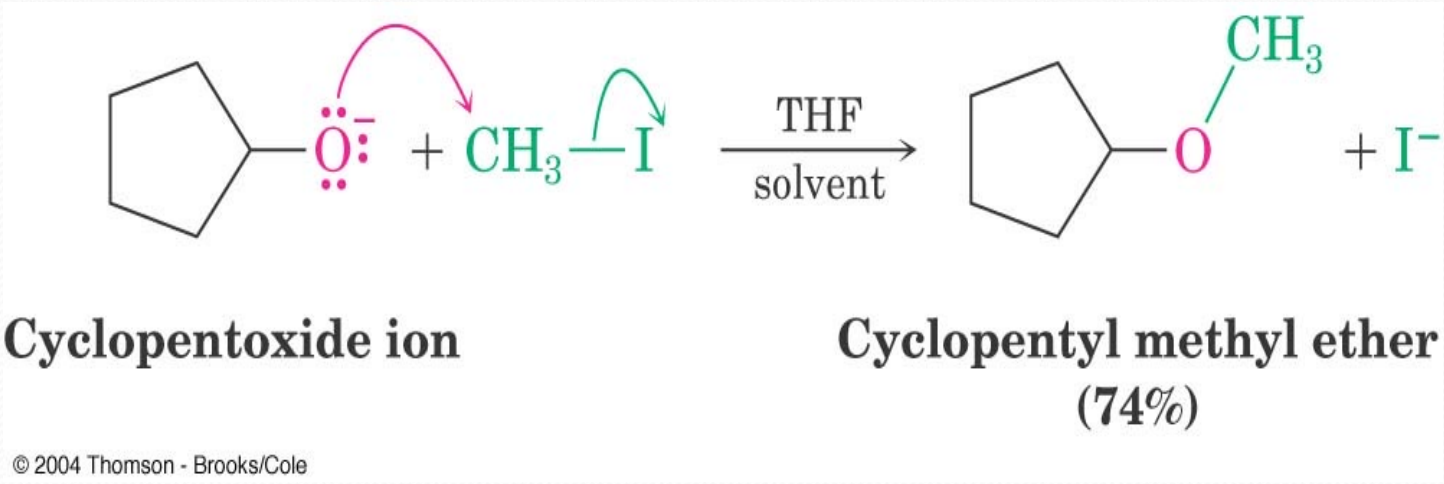
***p*-Dimethoxybenzene**



4-*tert*-Butoxy-1-cyclohexene

Williamson Ether Synthesis

- Reaction of metal alkoxides and primary alkyl halides and tosylates.
- Best method for the preparation of ethers.
- Alkoxides prepared by reaction of an alcohol with a strong base such as sodium hydride, NaH.

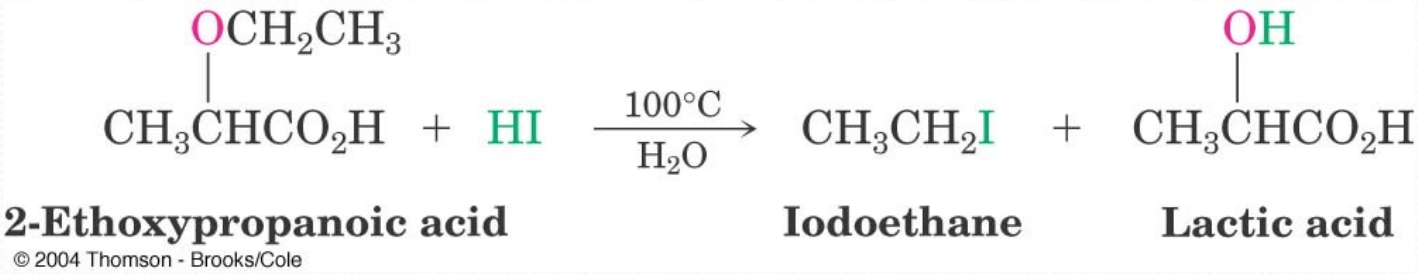


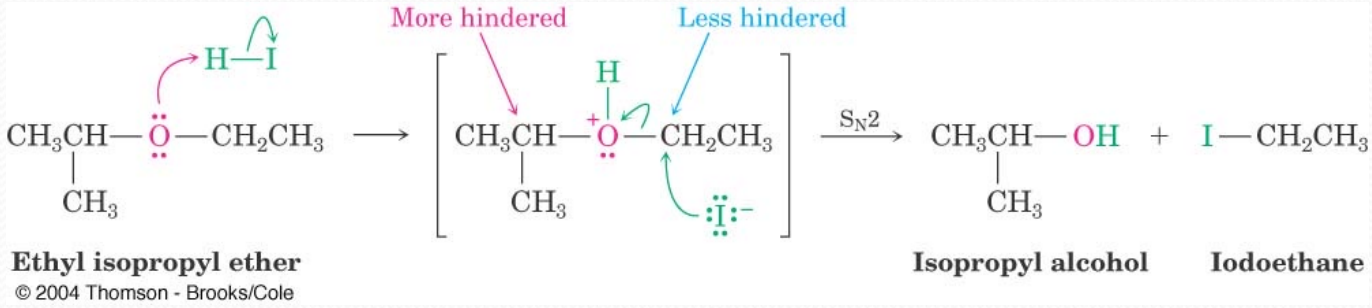
Cyclopentoxide ion

Cyclopentyl methyl ether (74%)

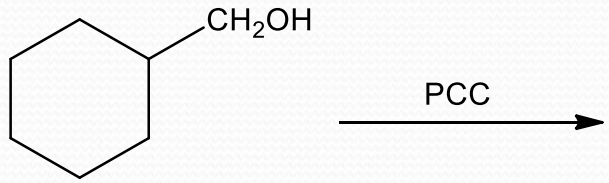
Reactions of Ethers:

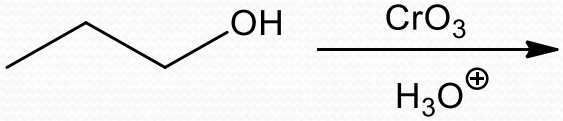
- Ethers are generally not reactive.
- Strong acid will cleave an ether at elevated temperature.

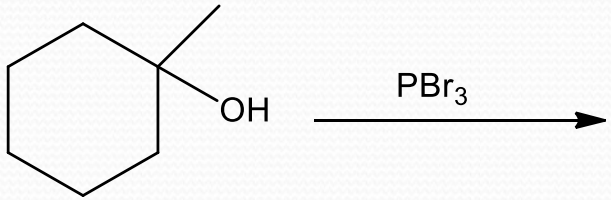


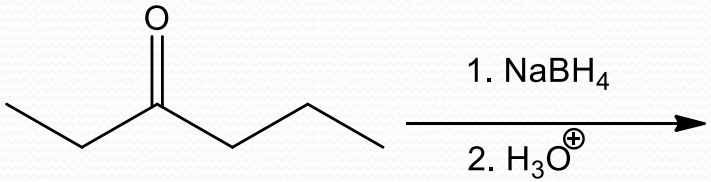


Practice Problems

1. 

2. 

3. 

4. 

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