

Chapter 8. Alcohols, Phenols, and Ethers

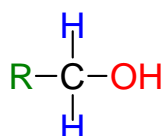
Alcohol: A compound that has a hydroxyl group ($-\text{OH}$) bonded to a saturated, sp^3 -hybridized carbon atom.

Phenol: A compound that has a hydroxyl group bonded to an aromatic ring.

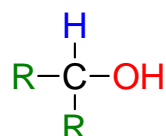
Ether: A compound that has an oxygen atom bonded to two organic groups.

8.1 Naming Alcohols, Phenols, and Ethers

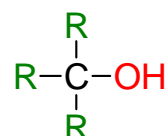
Alcohols



A primary alcohol (1°)



A secondary alcohol (2°)



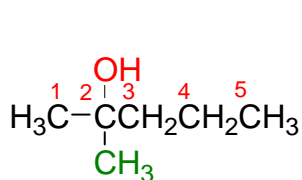
A tertiary alcohol (3°)

Simple alcohols are named in the IUPAC system as derivatives of the parent alkane, using the suffix ***-ol***.

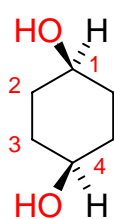
Step 1. Select the longest carbon chain containing the hydroxyl group, and replace the $-e$ ending of the corresponding alkane with $-ol$.

Step 2. Number the carbons of the parent chain **beginning at the end nearer the hydroxyl group**.

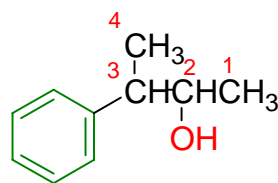
Step 3. Number all substituents according to their position on the chain, and write the name listing the substituents in **alphabetical order**.



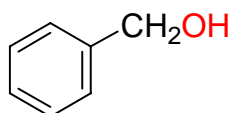
2-Methylpentan-2-ol



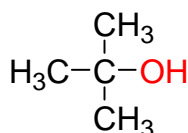
cis-cyclohexane-1,4-diol



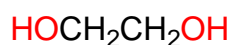
3-phenylbutan-2-ol



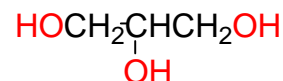
Phenylmethanol
(Benzyl alcohol)



2-Methylpropan-2-ol
(tert-Butyl alcohol)



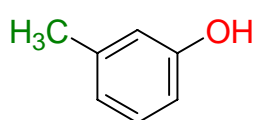
Ethane-1,2-diol
(Ethylene glycol)



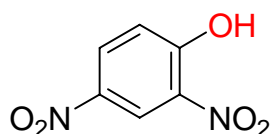
Propane-1,2,3-triol
(Glycerol)

Phenols

Phenols are named as substituted aromatic compounds with ***-phenol*** used as the parent name rather than $-\text{benzene}$.



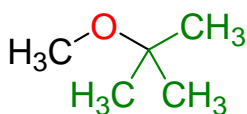
m-Methylphenol



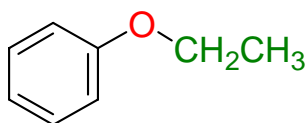
2,4-Dinitrophenol

Ethers

Simple ethers that contain no other functional groups are named by identifying the two organic groups and adding the word **ether**.

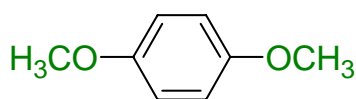


tert-Butyl methyl ether

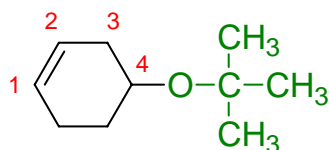


Ethyl phenyl ether

If more than one ether linkage is present, or if other functional groups are present, the ether part is named as an **alkoxy** substituent on the parent compound.



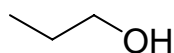
p-Dimethoxybenzene



4-*tert*-Butoxycyclohexene

8.2 Properties of Alcohols, Phenols, and Ethers: Hydrogen Bonding

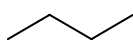
bp. 97.4 °C



C₃H₈O

Mol. Wt.: 60.10

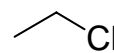
-0.5 °C



C₄H₁₀

Mol. Wt.: 58.12

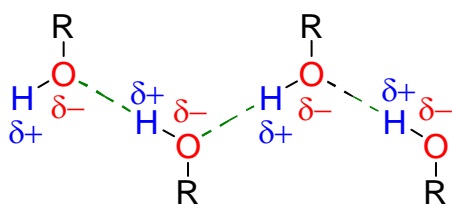
12.3 °C



C₂H₅Cl

Mol. Wt.: 64.51

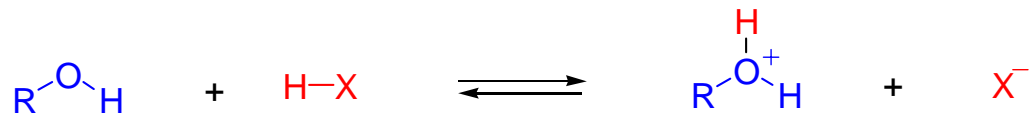
Alcohols and phenols have unusually **high boiling points** due to the **hydrogen bonding** in the liquid state. The positively polarized -OH hydrogen of one molecule is attracted to the negatively polarized oxygen of another molecule.



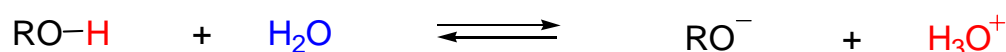
8.3 Properties of Alcohols and Phenols: Acidity

Alcohols and phenols are both weakly basic and weakly acidic.

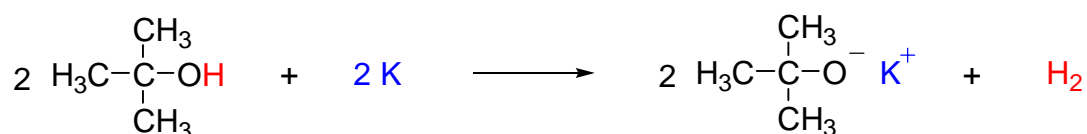
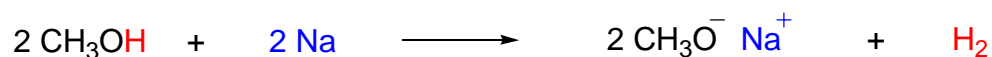
As weak bases, alcohols and phenols are reversibly protonated by strong acids to yield **oxonium ions**, ROH_2^+ .



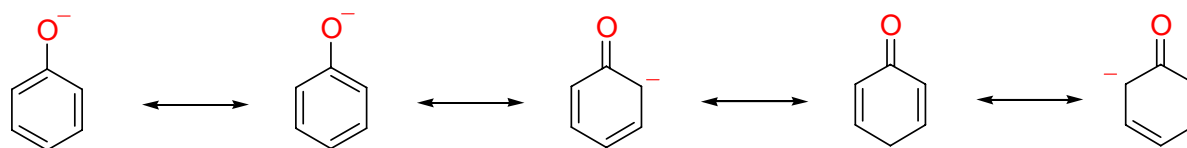
As weak acids, alcohols and phenols dissociate to a slight extent by donating a proton to water, generating H_3O^+ and an **alkoxide ion** (RO^-).



Alcohols react with alkali metals to yield **Metal alkoxide that are strong bases**.

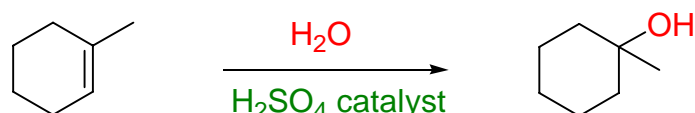


Phenols are about a million times more acidic than alcohols (phenols are soluble in dilute aqueous NaOH, but alcohols are not). Phenoxide anion is resonance-stabilized by the aromatic ring.



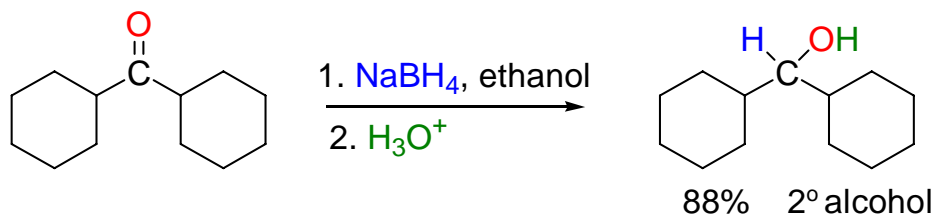
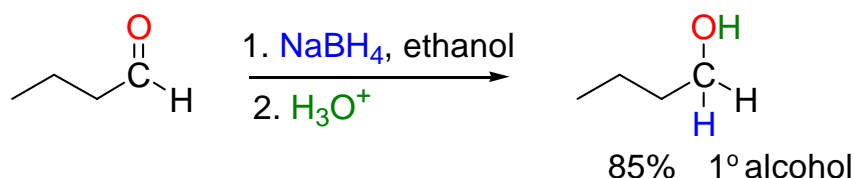
8.4 Synthesis of Alcohols

Alcohols can be prepared by hydration of alkenes following the Markovnikov rule.



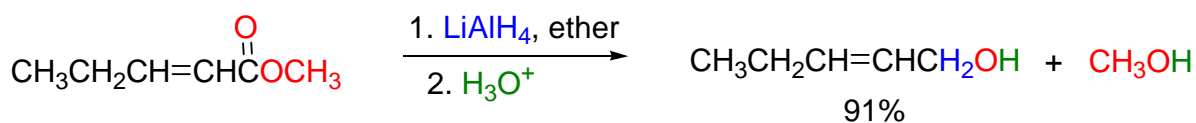
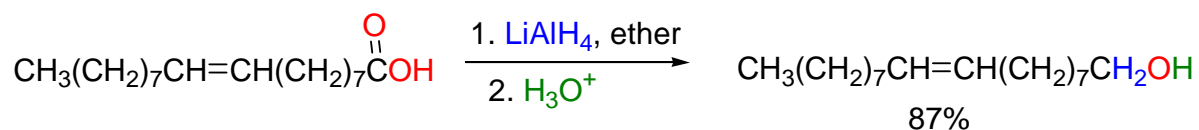
Reduction of Aldehydes and Ketones

Aldehydes are converted into primary alcohols, and ketones are converted into secondary alcohols. **Sodium borohydride**, NaBH_4 , is usually chosen because of its safety and ease of handling.



Reduction of Esters and Carboxylic Acids

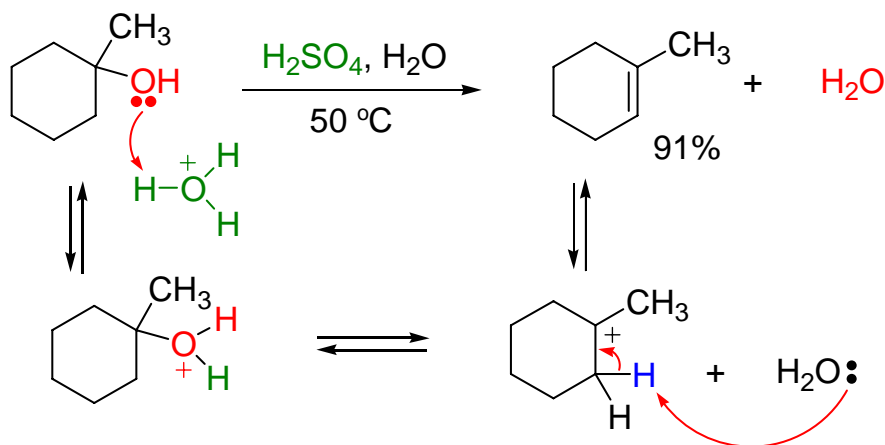
Esters and carboxylic acids are reduced to give **primary alcohols**. These reductions proceed more slowly than the corresponding reductions of aldehydes and ketones, so **the more powerful reducing agent LiAlH₄** is used. Two hydrogens are added to the carbonyl carbon during the reduction.



8.5 Reaction of Alcohols

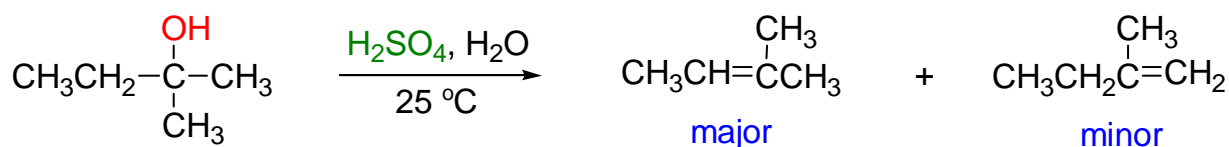
1. Dehydration of Alcohols – elimination of H₂O to give alkenes.

Treatment of secondary and tertiary alcohols with a strong acid.



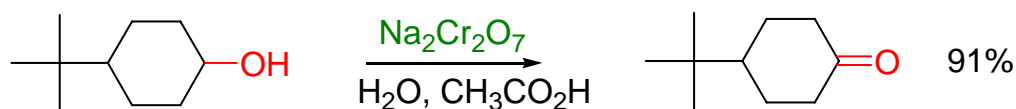
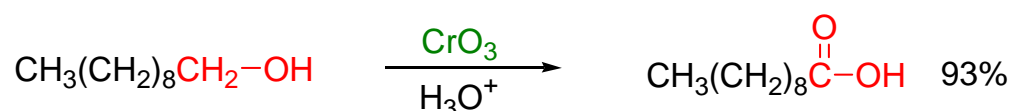
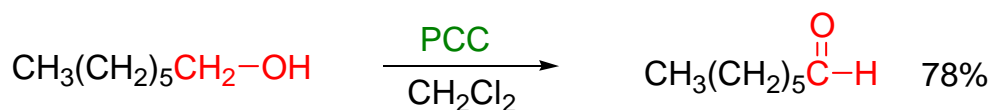
The mechanism is E1 process: Strong acid protonates the alcohol oxygen, the protonated intermediate spontaneously loses water to generate a carbocation, and a loss of H⁺ from the neighboring carbon atom yield the alkene product.

Acid-catalyzed dehydrations follow **Zaitsev's rule**, giving the more highly substituted alkene as major product.



2. Oxidation of Alcohols

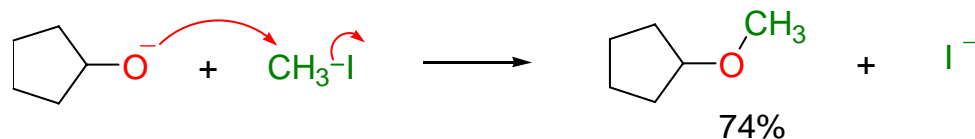
Primary alcohols give aldehydes (non-aqueous condition: PCC, PDC in CH_2Cl_2) or carboxylic acids (aqueous acidic condition), secondary alcohols give ketones, but tertiary alcohols don't normally react with oxidizing agents.



PCC: pyridinium chlorochromate ($\text{C}_5\text{H}_6\text{NCrO}_3\text{Cl}$)

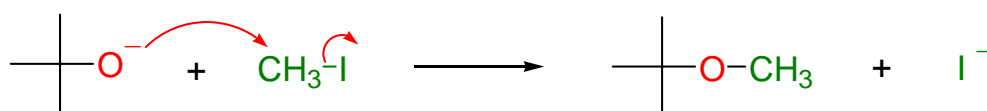
3. Conversion into Ethers

Williamson ether synthesis – Alcohols are converted into ethers by formation of the corresponding alkoxide ion followed by reaction with an alkyl halide ($\text{S}_{\text{N}}2$ process).

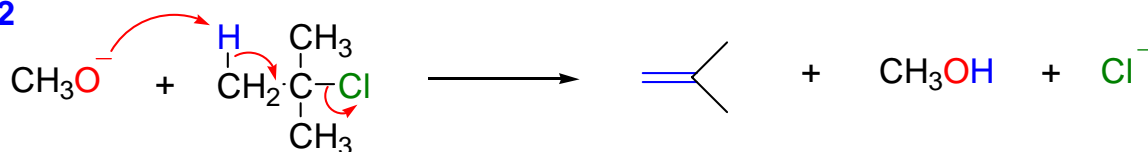


Reaction of the more hindered alkoxide with the less hindered alkyl halide works best.

$\text{S}_{\text{N}}2$



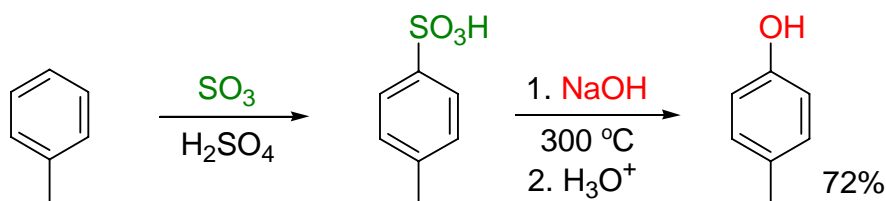
$\text{E}2$



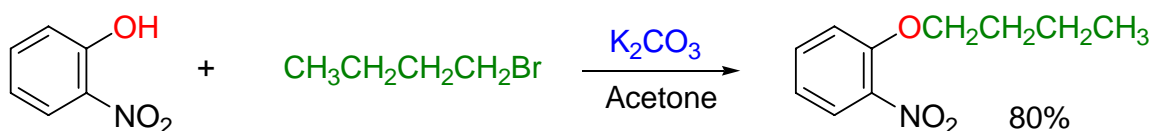
8.6 Synthesis and Reactions of Phenols

Synthesis of Phenols

An aromatic compound is first sulfonated by treatment with $\text{SO}_3/\text{H}_2\text{SO}_4$, and the resulting sulfonic acid is then converted into a phenol by high-temperature reaction with NaOH .



1. Alcohol-Like Reactions of Phenols

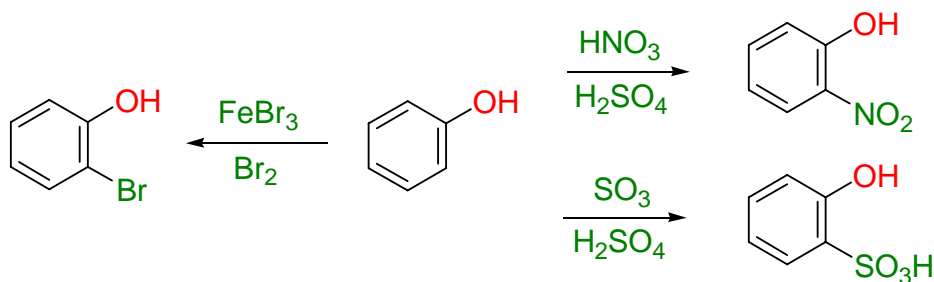


However, phenols can't be dehydrated by treatment with acid and can't be converted into halides by treatment with HX .

2. Electrophilic Aromatic Substitution Reactions of Phenols

The $-\text{OH}$ group is an activating, ortho- and para-directing substituent in electrophilic aromatic substitution reactions.

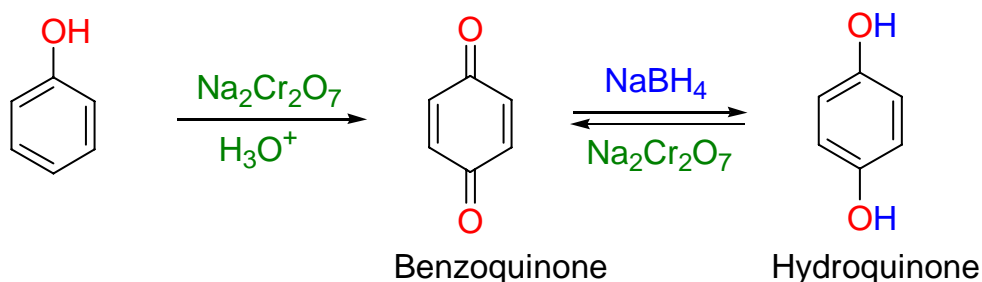
Halogenation, Nitration, and Sulfonation.



3. Oxidation of Phenols: Quinones

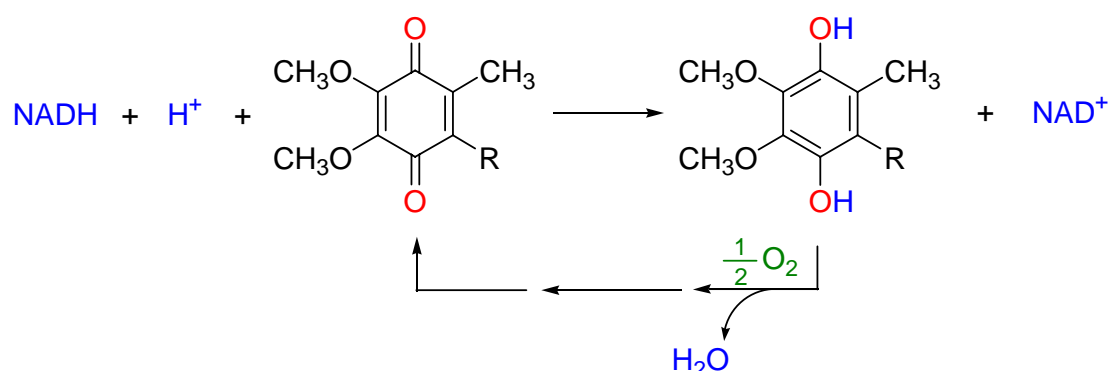
Treatment of a phenol with a strong oxidizing agent such as sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) yields a cyclohexadienedione, or **quinone**.

Quinones can be easily reduced to **hydroquinones** (*p*-dihydroxybenzenes) by NaBH_4 or SnCl_2 , and hydroquinones can be easily oxidized back to quinones by $\text{Na}_2\text{Cr}_2\text{O}_7$.



Ubiquinones – biochemical oxidizing agents in electron-transfer processes.

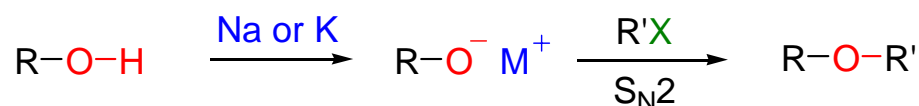
Ubiquinones mediate the respiration process in which electrons are transported from NADH to molecular oxygen to give NAD^+ and water. Energy is produced through the process.



8.7 Synthesis and Reactions of Ethers

Synthesis of Ethers

Conversion of alcohols to alkoxide ions followed by $\text{S}_{\text{N}}2$ reaction with a primary alkyl halide.



Reactions of Ethers

Ethers are unreactive to most common reagents (halogens, mild acids, bases, and nucleophiles) – ethers are widely used as **reaction solvents**.

Ethers are cleaved by strong acids such as aqueous HI or HBr by either an **$\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ pathway**, depending on the structure of the ether.

You can tell the mechanism by the product analysis.

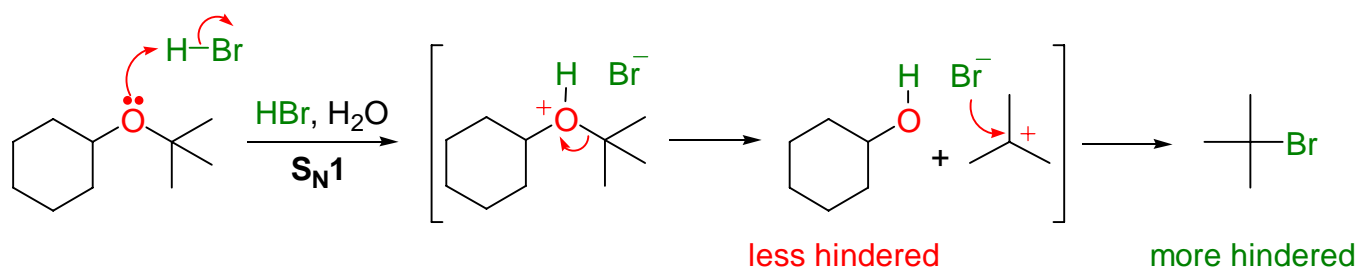
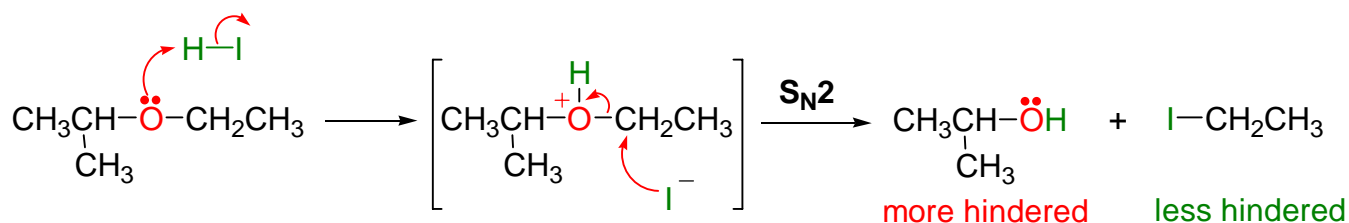
$\text{S}_{\text{N}}2$ cleavage – primary and secondary alkyl groups

Nucleophilic halide ion attacks the protonated ether at the less hindered site. *The ether oxygen atom* stays with the more hindered alkyl group.

S_N1 cleavage – tertiary alkyl groups (stable carbocation intermediates)

The ether oxygen atom stays with the less hindered alkyl group, and the halide bonds to the tertiary group.

Examples



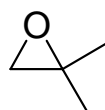
8.8 Epoxides

Angle strain in the three-membered ring gives higher reactivity than acyclic ethers.

Naming

Use the name of the parent alkene followed by **oxide**, or

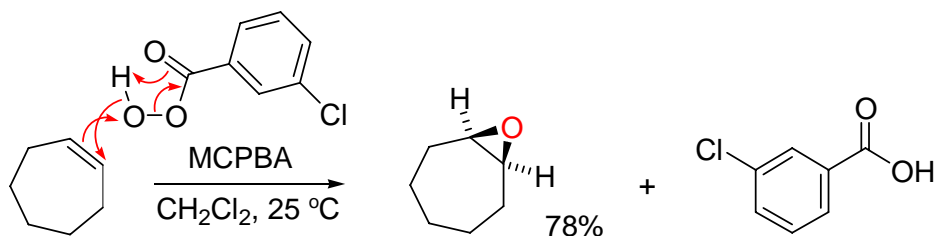
Use the name of the parent alkane with an “**epoxy**” prefix.



propylene **oxide** ethylene **oxide** 1,2-**epoxy**-2-methylpropane 1,2-**epoxy**butane

Preparation

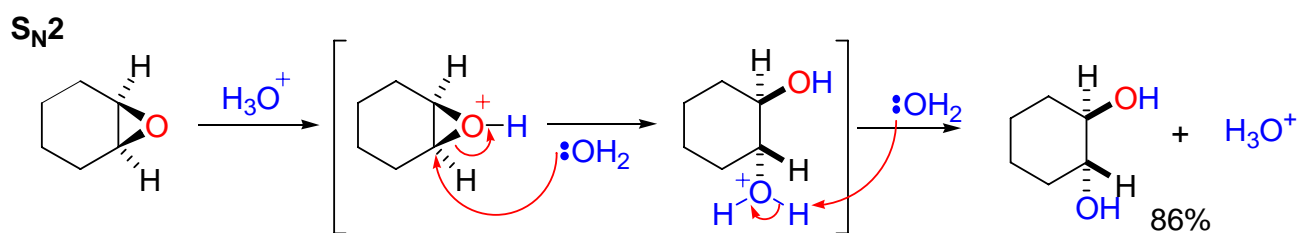
Reaction of an alkene with a peroxyacid, RCO₃H.



Reaction

Ring cleavage by dilute aqueous acid to give a 1,2-diol.

Acid-catalyzed epoxide cleavage takes place by S_N2 attack of H₂O on the protonated epoxide.

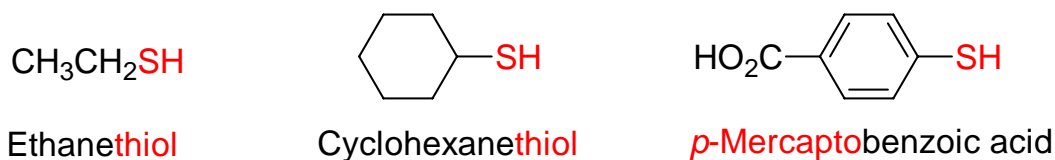


8.9 Thiols and Sulfides

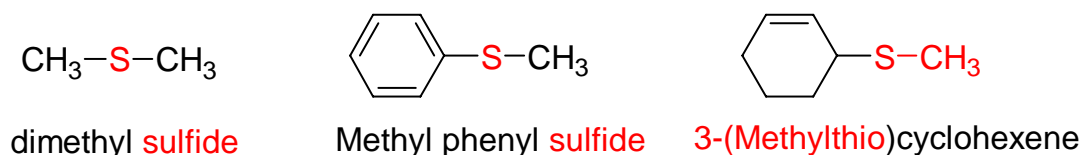
Thiols, $R-SH$, are sulfur analogs of alcohols; **sulfides**, $R-S-R'$, are sulfur analogs of ethers.

Naming

Thiols are named in the same way as alcohols, with the suffix **-thiol** used in place of **-ol**. The $-SH$ group is referred to as a **mercapto group**.

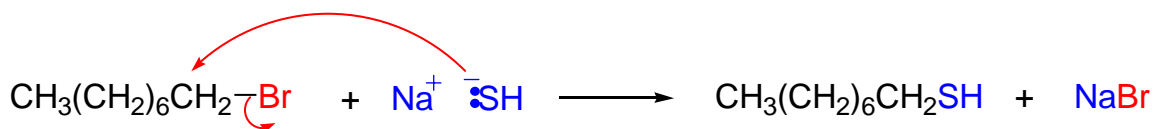


Sulfides are named in the same way as ethers, with **sulfide** used in place of **ether**. The prefix **alkylthio** is used in place of **alkoxy** for more complex substances.

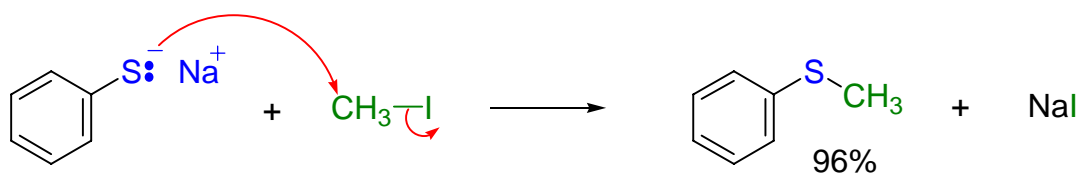


Preparation

Thiols can be prepared by the S_N2 reaction of **hydrosulfide anion**, SH^- , with alkyl halide.



Sulfides are prepared by treating a primary or secondary alkyl halide with a **thiolate ion**, RS^- .



Thiols can be oxidized by bromine to yield disulfides, and disulfides can be reduced back to thiols by treatment with zinc metal and acetic acid.

