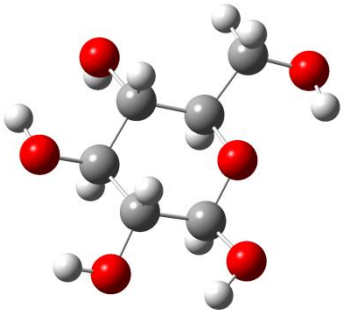
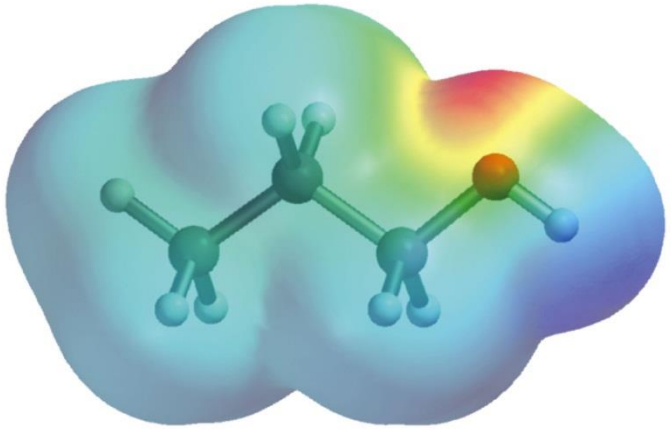
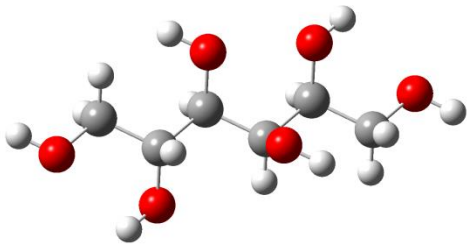




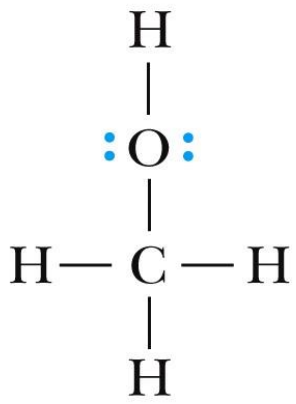
Chapter 7: Alcohols, Phenols and Thiols



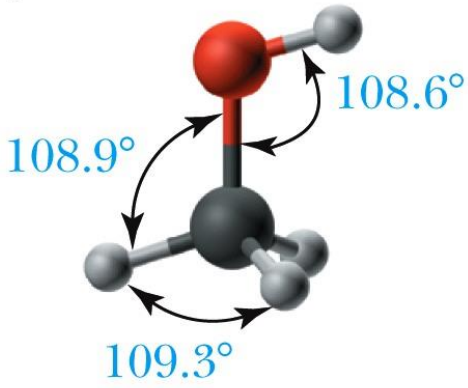
Alcohols - Structure

- The functional group of an alcohol is an -OH (hydroxyl) group bonded to an sp^3 hybridized carbon.
  - Bond angles about the hydroxyl oxygen atom are approximately 109.5°.
- Oxygen is also sp^3 hybridized.
  - Two sp^3 hybrid orbitals form sigma bonds to carbon and hydrogen.
  - The remaining two sp^3 hybrid orbitals each contain an unshared pair of electrons.

(a)



(b)

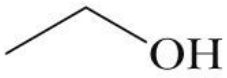


Alcohols - Nomenclature

- IUPAC names
  - The parent chain is the longest chain that contains the -OH group.
  - Number the parent chain in the direction that gives the -OH group the lower number.
  - Change the suffix **-e** to **-ol**.
- Common names
  - Name the alkyl group bonded to oxygen followed by the word **alcohol**.

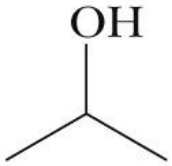
Alcohols - Nomenclature

- Examples:



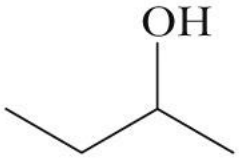
Ethanol
(Ethyl alcohol)

1-Propanol
(Propyl alcohol)

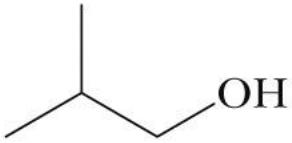


2-Propanol
(Isopropyl alcohol)

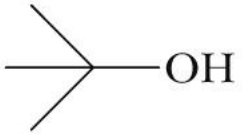
1-Butanol
(Butyl alcohol)



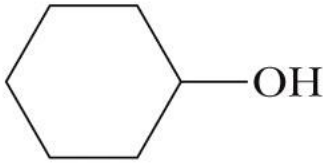
2-Butanol
(*sec*-Butyl alcohol)



2-Methyl-1-propanol
(Isobutyl alcohol)

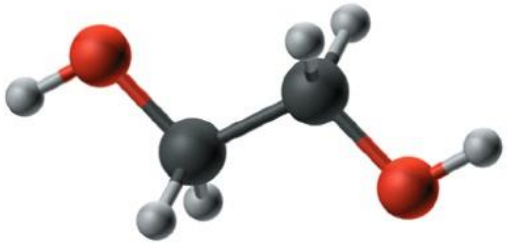


2-Methyl-2-propanol
(*tert*-Butyl alcohol)



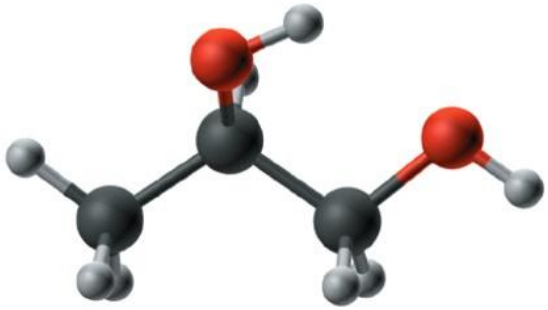
Cyclohexanol
(Cyclohexyl alcohol)

Alcohols - Nomenclature

- 

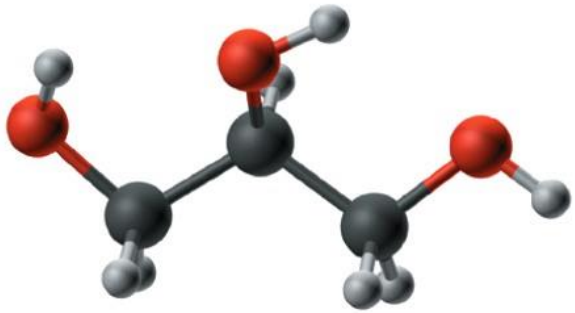
CH_2CH_2
| |
OH OH

1,2-Ethanediol
(Ethylene glycol)



CH_3CHCH_2
| |
HO OH

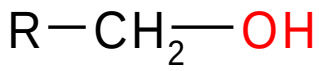
1,2-Propanediol
(Propylene glycol)



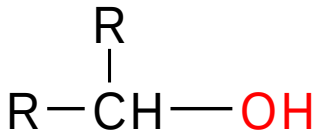
CH_2CHCH_2
| | |
HO HO OH

1,2,3-Propanetriol
(Glycerol, Glycerin)

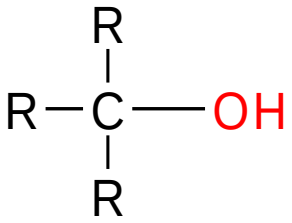
Classification of Alcohols



primary (1°) alcohol



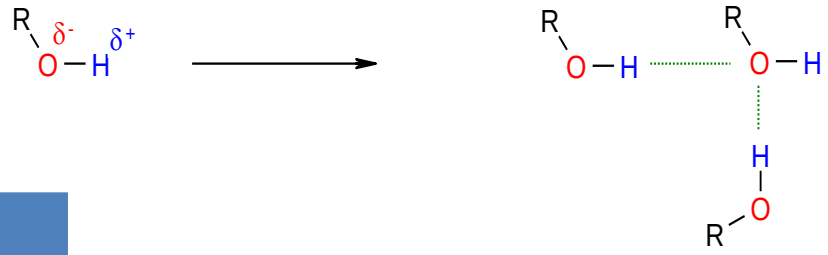
secondary (2°) alcohol



tertiary (3°) alcohol

Hydrogen Bonding in Alcohols

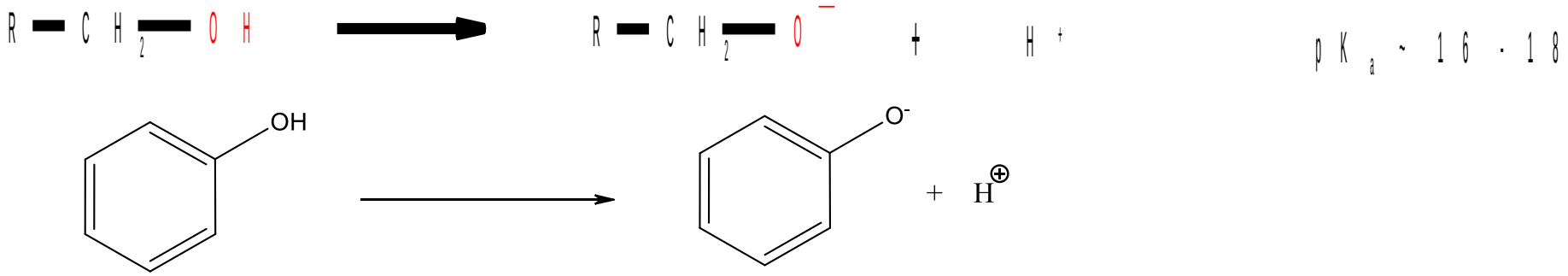
The presence of the OH group allows for H-bonding between alcohol molecules. This effects BP/MP and solubility, i.e.



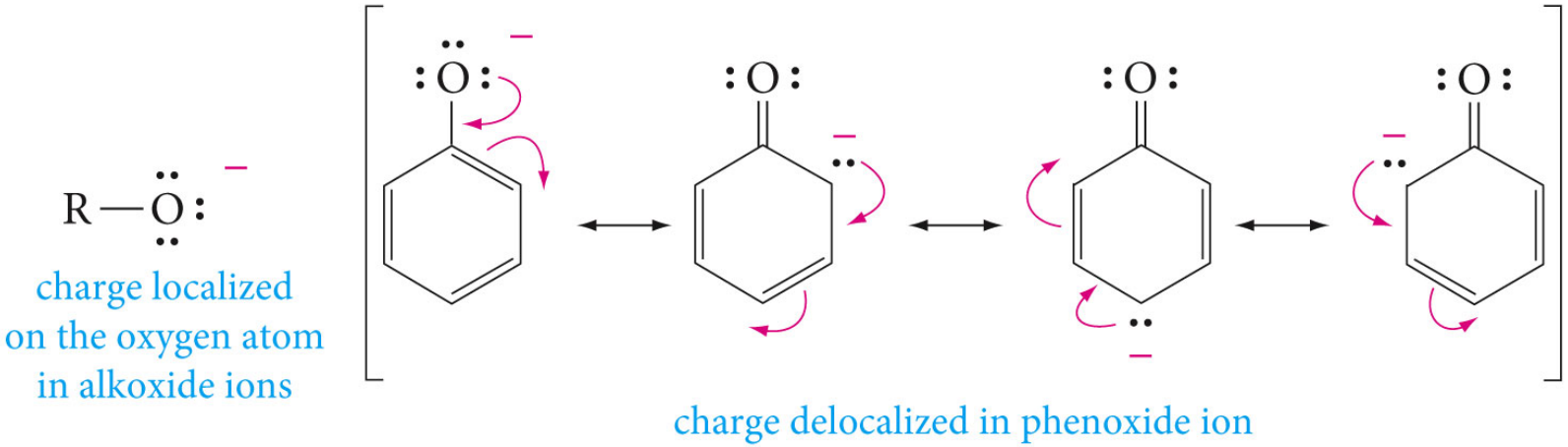
Alcohol	BP (°C)	Solubility (g/100 g H^2O)
Methanol	65	Completely soluble
Ethanol	78.5	Completely soluble
Propanol	97	Completely soluble
Butanol	117.7	7.9
Pentanol	137.9	2.7
Hexanol	155.8	0.59

Acidity of Alcohols and Phenols

Alcohols are weak acids similar to water, i.e.

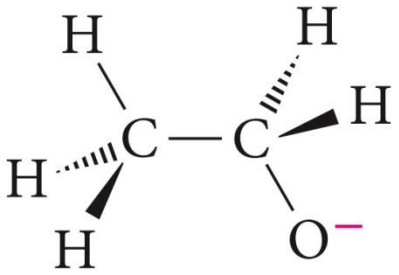


Phenols are more acidic as the conjugate base (a phenoxide ion) can to stabilized by resonance, i.e



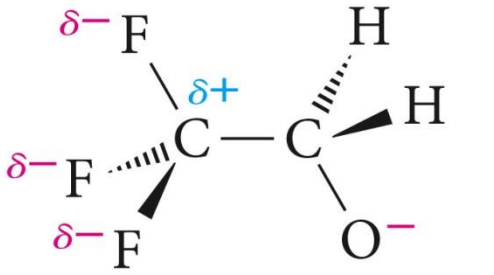
Acidity of Alcohols and Phenols

The acidity can be increased by electron withdrawing groups at the α-carbon on an alcohol, or on the aromatic ring at the o,p-positions, i.e.



ethoxide ion

pK_a ~ 16

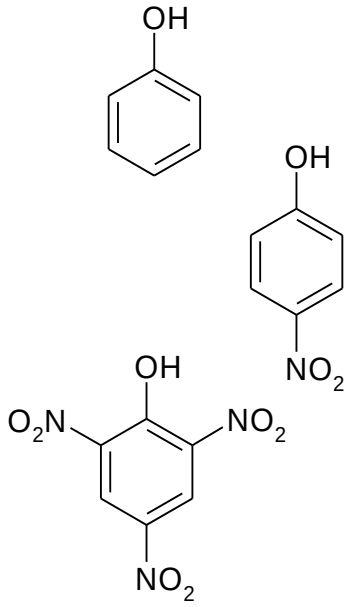


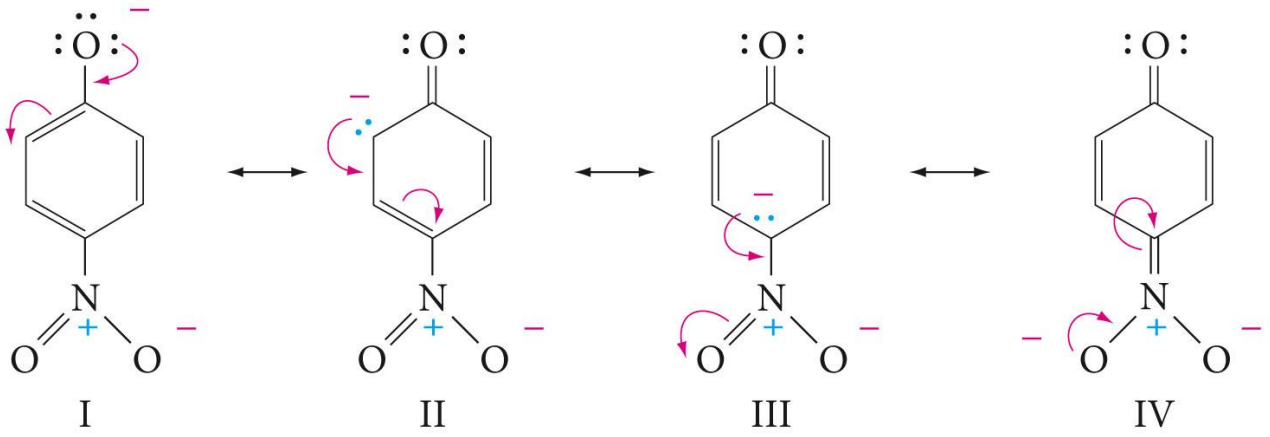
2,2,2-trifluoroethoxide ion

pK_a ~ 12.4

Acidity of Alcohols and Phenols

And for phenols:	(pK_a)
phenol	10.0
p-nitrophenol	7.2
picric acid	0.25



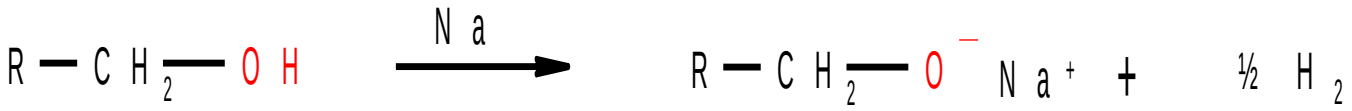


p-nitrophenoxide ion resonance contributors

Acidity of Alcohols and Phenols

Alkoxides are commonly used as strong bases. They are prepared by:

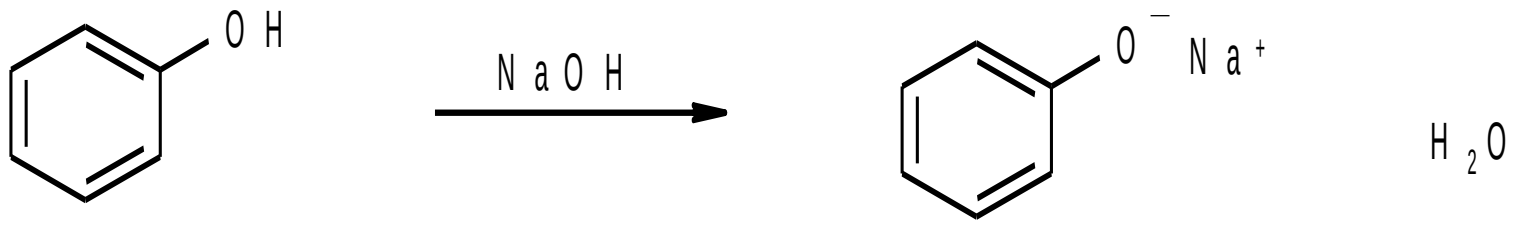
1) treating an alcohol with Na or K:



2) treating with NaH or KH (metal hydride)

Acidity of Alcohols and Phenols

Phenoxide can be produced by treating with NaOH since it is a stronger acid than an alcohol (which will not react with NaOH).

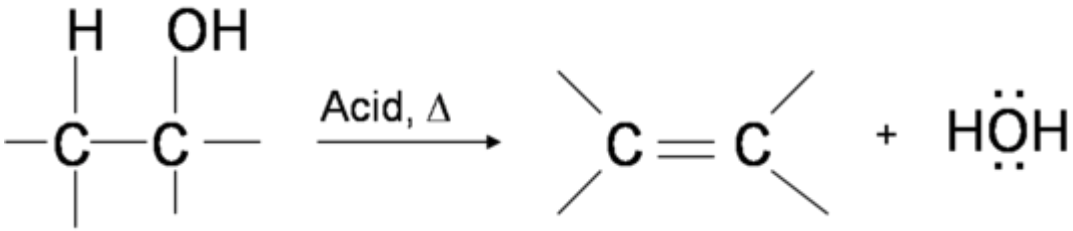


Dehydration of Alcohols

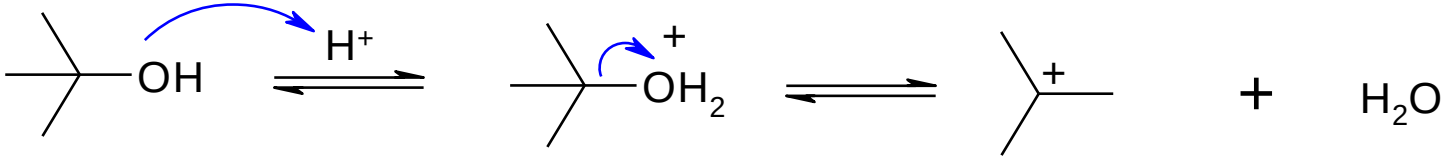
This is an ***elimination reaction*** and produces an alkene. It requires an acid catalyst (usually sulfuric acid) and heat, especially for less reactive 1° and 2° alcohols.

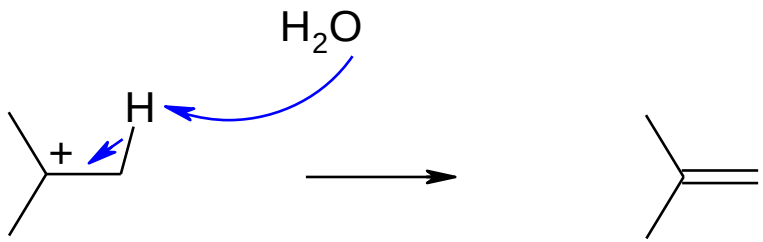
- 3° > 2° > 1° for reaction rate.
- Product: follows ***Zaitsev's rule***: more highly substituted alkene is the major product.
- 1st step is a rapid acid-base reaction.

Dehydration of Alcohols



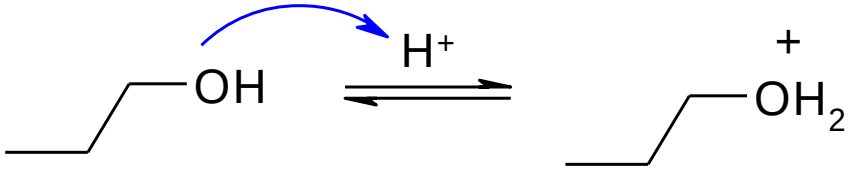
E1 mechanism: 3° alcohols, intermediate carbocation

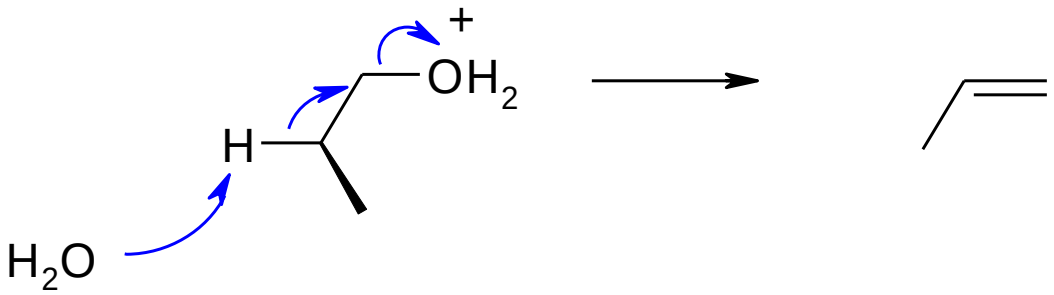




Dehydration of Alcohols

E2 mechanism: 1° alcohols, no intermediate carbocation, anti-periplanar





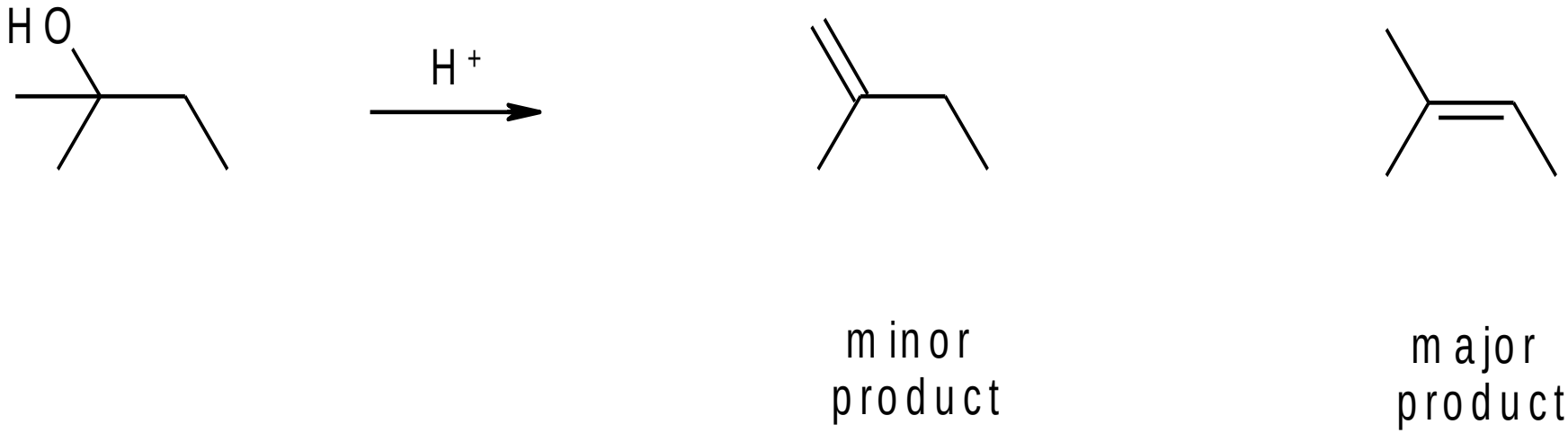
Dehydration of Alcohols

2° alcohols can react by either mechanism

E1 or E2 for dehydration usually produce the same products, but for E2 need an anti-periplanar H atom.

Dehydration of Alcohols

Zaitsev's rule:



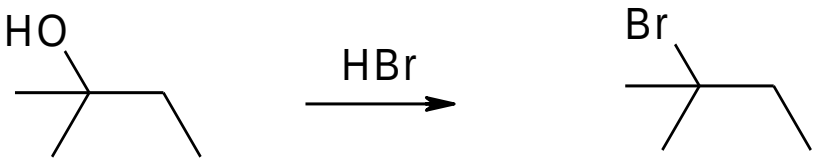
Reactions with Hydrogen Halides

The hydrogen halides are acids so they will protonate the OH group to generate water, an excellent leaving group.

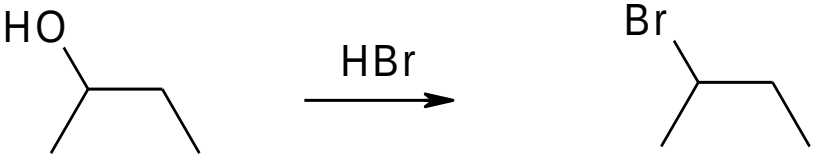
However the halide atom is nucleophilic so we get an *nucleophilic substitution* rather than an elimination.

Reactions with Hydrogen Halides

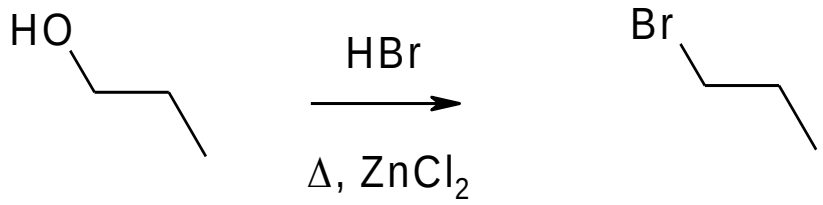
By type of alcohol:

3° 

S_N1 fast at RT

2° 

Both S_N1 & S_N2 intermediate temps

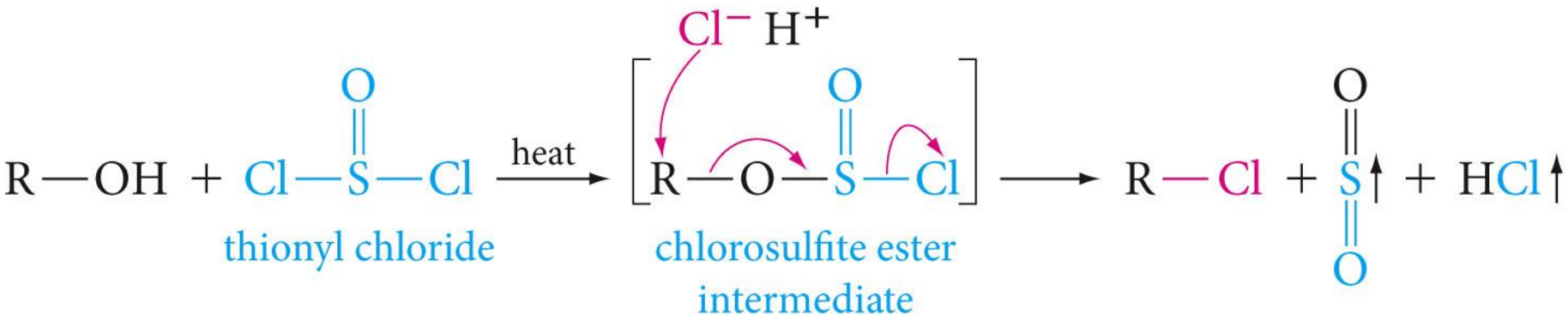
1° 

S_N2 slow requires heat and a $ZnCl_2$ catalyst

Other Routes to Alkyl Halides

Alkyl halides can also be generated from alcohols by:

1) *Thionyl chloride* (Cl_2SO):

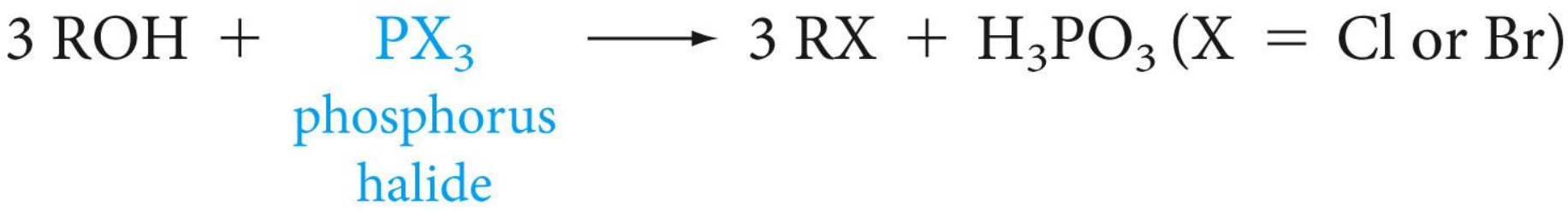


Advantageous as HCl and SO_2 are both gasses so help "drive" the reaction forward when they bubble out of solution. Not useful for small alkyl halide as they have too low a BP.

Other Routes to Alkyl Halides

Alkyl halides can also be generated from alcohols by:

2) *Phosphorus halides* (PX_3):



The phosphoric acid has a high BP so the alkyl halide can be separated by distillation.

Other Routes to Alkyl Halides

Both of these methods are used for 2° and 1° alcohols whose reaction with HX is slow.

None of these methods work with phenols as the phenol will not lose water (it can not form an sp hybridized C atom in such a small ring).

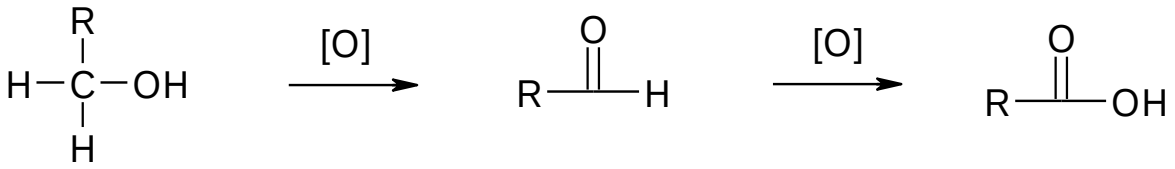
Oxidation of Alcohols

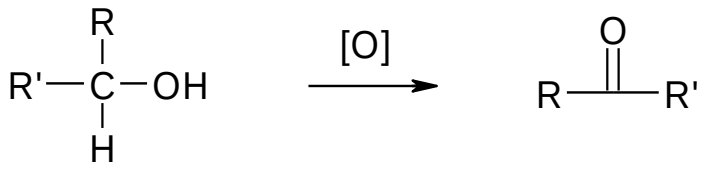
Oxidation is the process of increasing the positive charge on the C atom. This means increasing the number of bonds to more electronegative atoms such as O.

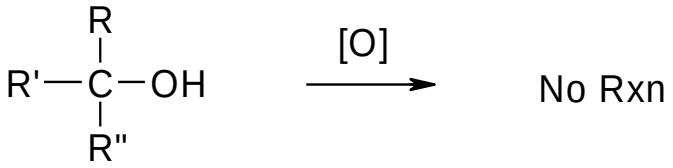
Oxidizing agent: is the chemical used to oxidized the alcohol, which itself is reduced. Most common oxidizing agents are chromium oxides (CrO_3 or $Cr_2O_7^{2-}$).

Oxidation of Alcohols

Oxidation of an alcohol requires at least one H atom attached to the carbon the OH is attached to, i.e.

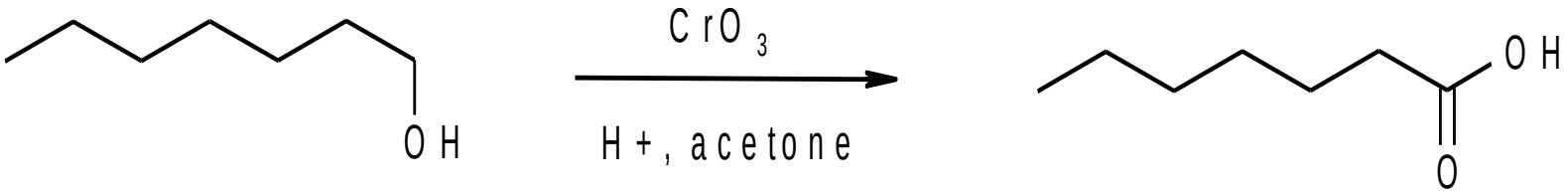


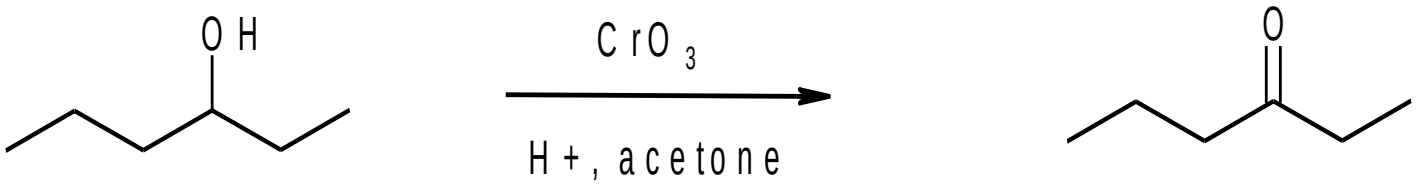




Oxidation of Alcohols

Common lab reagents are ***Jones' reagent*** (CrO_3 dissolved in aqueous sulfuric acid) in acetone, i.e.

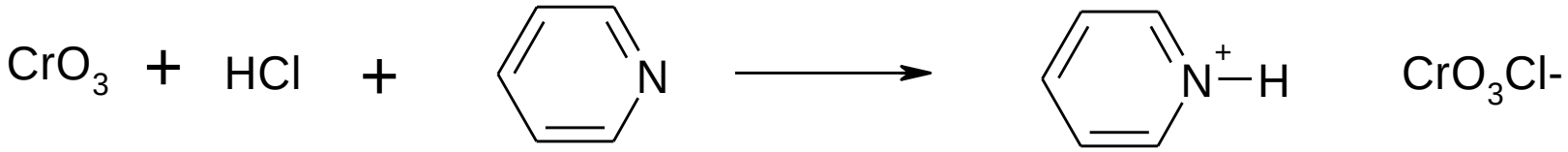


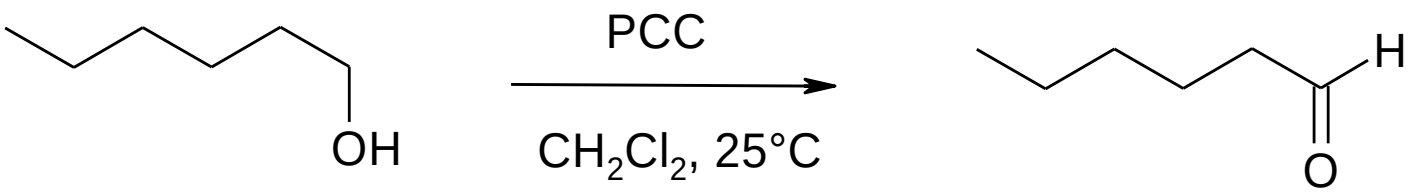


Note: oxidation of 1° alcohol produces an acid!

Oxidation of Alcohols

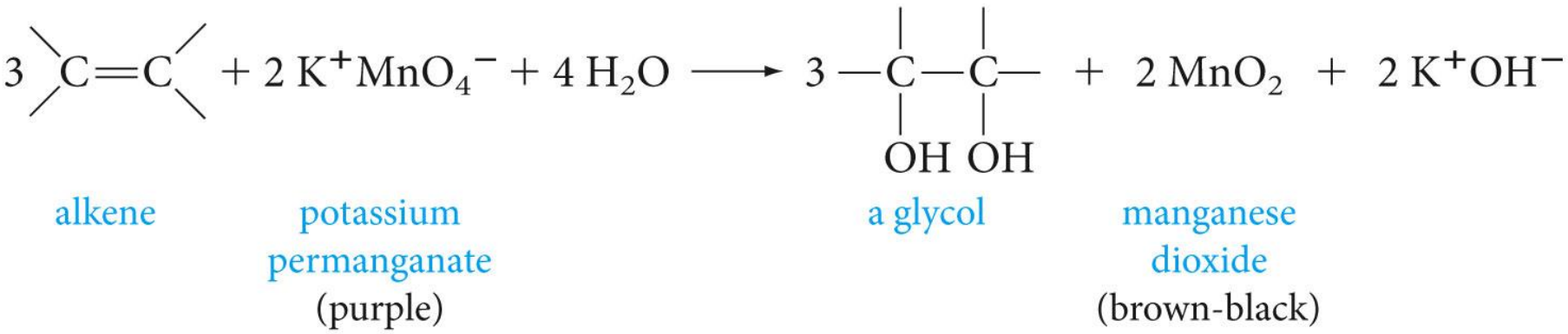
Oxidation of a 1° alcohol can be stopped at an aldehyde using ***pyridinium chlorochromate*** (PCC), i.e.





Oxidation of Alcohols

Note: $KMnO_4$ can also be used to oxidize alcohols but it is not selective for the OH group, C-C multiple bonds will also be oxidized.



Polyols: glycols

Glycols are molecules with more than one OH group, i.e. a multiple alcohol.

They are characterized by very high BP, and are very water soluble.

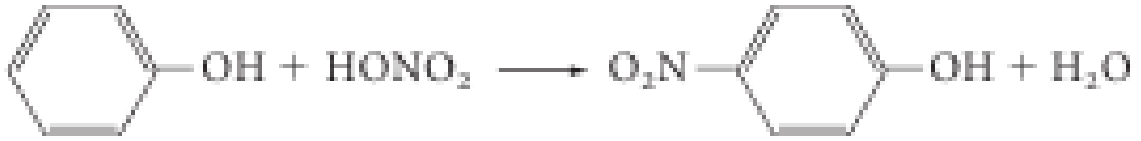
ethylene glycol
(1,2-ethanediol)
bp 198°C

glycerol (glycerine)
(1,2,3-propanetriol)
bp 290°C (decomposes)

sorbitol
(1,2,3,4,5,6-hexanehexaol)
mp 110–112°C

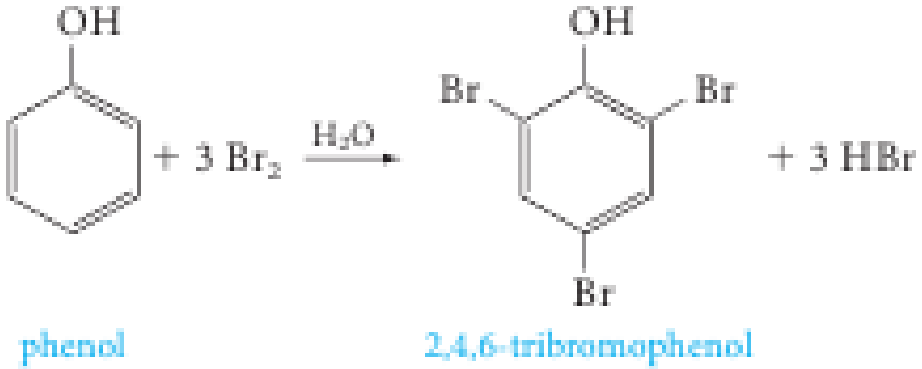
Phenols

In aromatic substitution reactions the OH group is activating and o,p-directing, thus subsequent reactions are fast and easy to do.



(7.42)

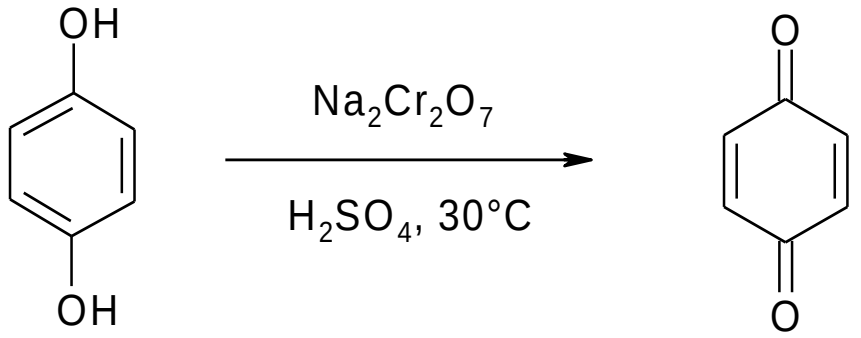
Phenol is also brominated rapidly with *bromine* in water, to produce 2,4,6-tribromophenol.



(7.43)

Oxidation of Phenols

Quinones and Hydroquinones are naturally occurring phenols used in redox reactions in the cell, i.e.



hydroquinone

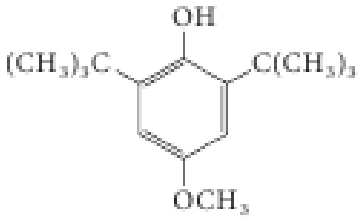
1,4-benzoquinone

ubiquinone or Co Q_{10}

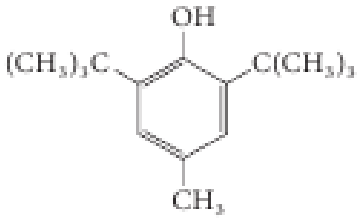
7.16 Phenols as Antioxidants

Substances that are sensitive to air oxidation, such as foods and lubricating oils, can be protected by phenolic additives. Phenols function as **antioxidants**. They react with and destroy peroxy (ROO·)and hydroxy (HO·) radicals, which otherwise react with the alkenes present in foods and oils to cause their degradation. The peroxy and hydroxy radicals abstract the phenolic hydrogen atom to produce more stable phenoxy radicals that cause less damage to the alkenes (eq. 7.45).

(7.45)



BHA



BHT

Thiols

The striped skunk (*Mephitis mephitis*) sprays a foul mixture of thiols at its enemies.

Sulfur analog of an alcohol, i.e. R-SH

- SH is a sulfhydryl or sulfanyl group.

Sulfur is immediately beneath oxygen in the periodic table and can often take its place in organic structures. The —**SH** group, called the **sulfhydryl group**, is the functional group of thiols (page 207). Thiols are named as follows:

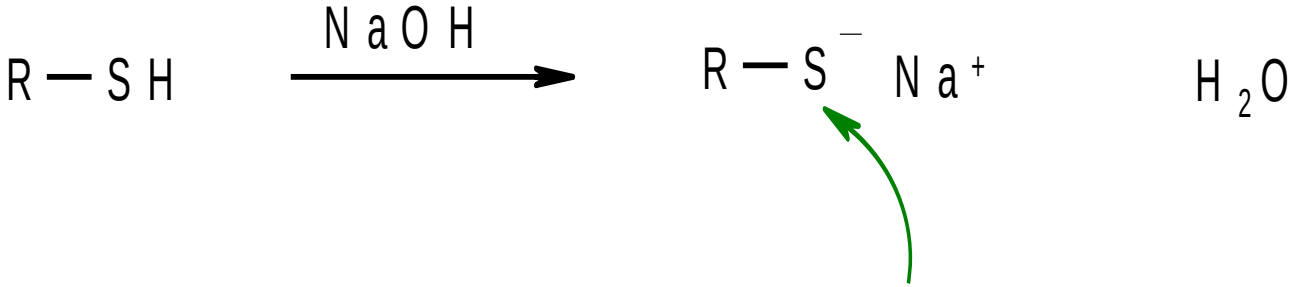
methanethiol (methyl mercaptan)

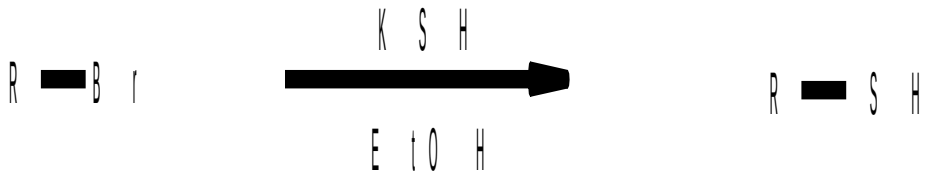
1-butanethiol (*n*-butyl mercaptan)

thiophenol (phenyl mercaptan)

Thiols

- S is larger than an O atom so forms a more stable anion, as a result it is more acidic than an alcohol.





Thiols can be made from alkyl halides treated with KSH, potassium hydrosulfide.

Thiols

Thiols are easily oxidized to disulfides, this provides cross-linking in proteins and synthetic rubber compounds (vulcanization).

[O] is H_2O_2 or I_2