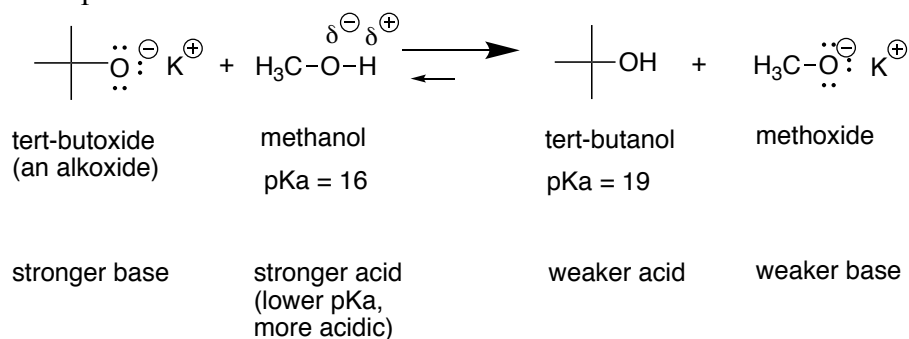
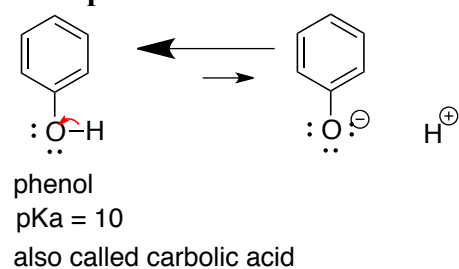
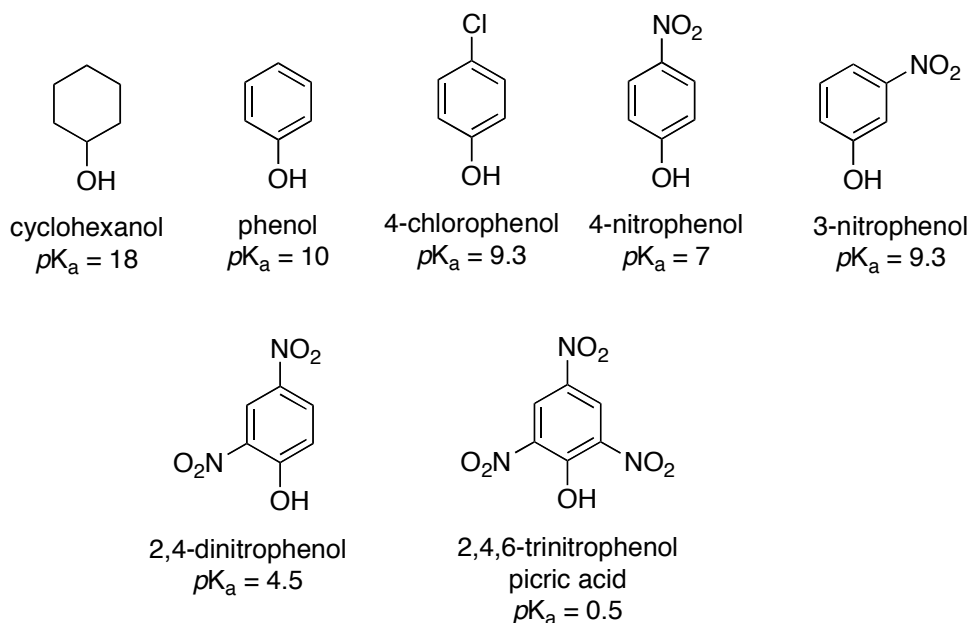


REVIEW:

Example:

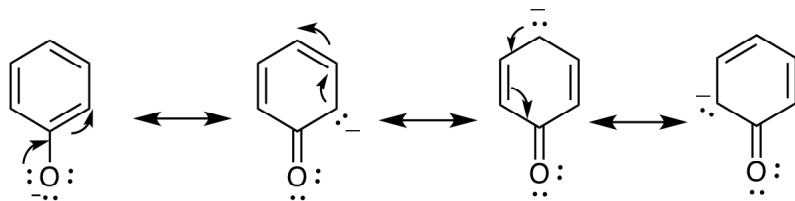


Example:

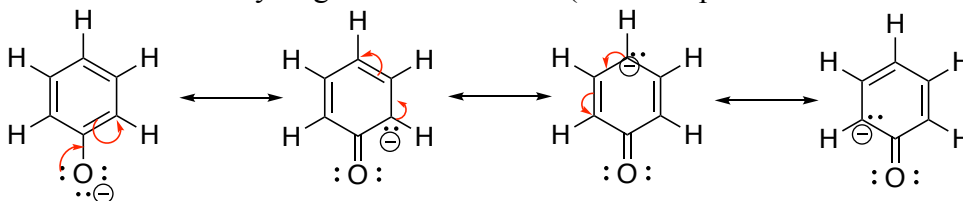
**Acidity of alcohols continued ...**

What is the influence of substituents? inductive & resonance

As the pK_a values above show, phenol is 10^8 more acidic than cyclohexanol.



Or if we show the hydrogen atoms attached (similar representation as above)

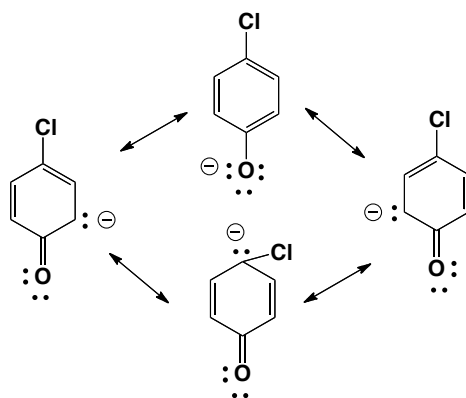


Phenol has a pK_a value of 10 (given this information, you should immediately recognize that it is much more acidic (about 6 orders of magnitude) than water (pK_a 15.7) and methanol (pK_a 16) since it has lower pK_a value). As phenol is more acidic, this means that its conjugate anion is more stable. The phenoxide anion is stabilized through resonance (shown above). It has 4 resonance forms, and therefore, more ability to spread the negative charge and be stabilized.

Where does the equilibrium lie for ionization of phenol to phenoxide and a proton (H^+) ?

Answer: It lies far to the left (not ionized). Even though phenol is 10^6 more acidic than water, its pK_a of 10 tells you that the acidity constant is 10^{-10} or that only one part in 10^{10} is ionized; the rest exists as phenol with H attached to oxygen.

Example: Chlorophenol

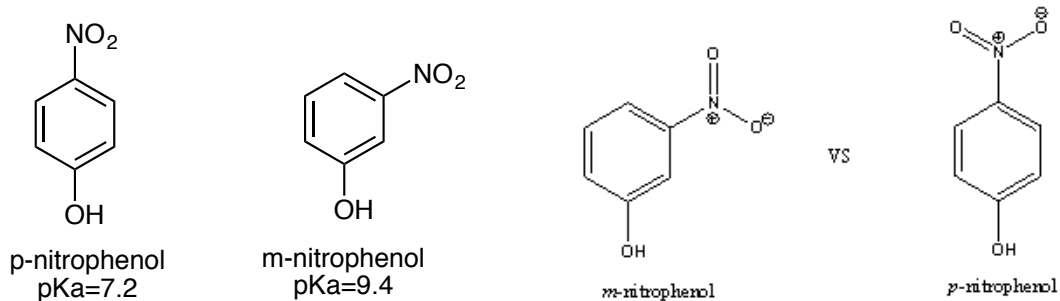


Is the anion more or less stabilized compared to phenol?

Answer: More stabilized. The chlorine atom is electron withdrawing, and stabilizes the negative charge at the *para* position through the inductive withdrawing effect. However, it also has a weak resonance donating effect. The inductive effect of chlorine wins over

resonance effect in this case (contrast this with electrophilic aromatic substitution where the resonance donating effect wins out against the inductive effect).

Example: *para*- and *meta*-nitrophenol



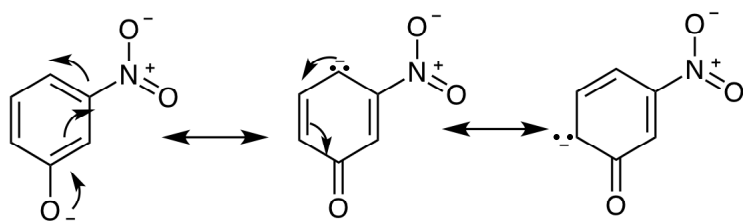
p-nitrophenol has a pK_a value of 7.2, whereas *m*-nitrophenol has a pK_a value of 9.3

Which one is more acidic?

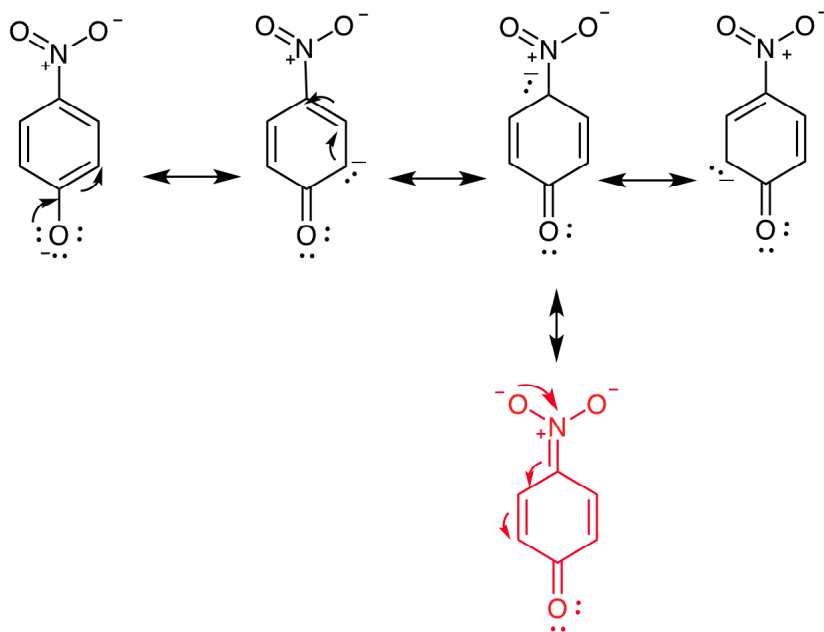
Answer: *p*-nitrophenol

Why? (Think about conjugate anion stabilization and resonance forms).

Resonance forms for *m*-nitrophenoxide anion:



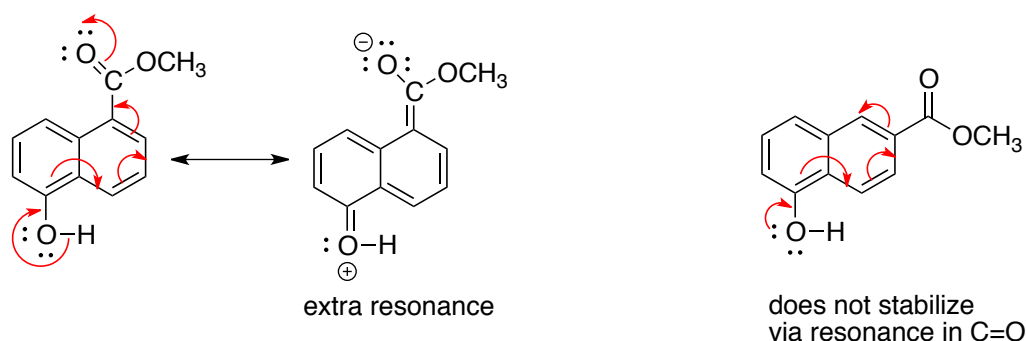
Resonance forms for *p*-nitrophenoxide anion:



The nitro group offers an additional resonance form for *p*-nitrophenol that is not possible for *m*-nitrophenol (we are able to drive electrons all the way in to the nitro group for the *para*-substituted nitrophenol). Since there is an additional reasonable resonance form, the *p*-nitrophenol pK_a 7.2 is about 100 times (10^2) more acidic than the *m*-nitrophenol with pK_a 9.3 (pK_a 9.3-7.2 = 2.1 pK_a units)

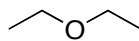
If there are two nitro groups in the *ortho* and *para* positions of the phenoxide anion, the pK_a of the phenol (2,4-dinitrophenol) drops to 4.5. If three nitro groups are attached, the pK_a of the phenol becomes even lower (2,4,6-trinitrophenol has a pK_a of approximately 0.5). This is because *ortho* and *para* positions are where the negative charge of the resonance form can be located, and addition of a nitro group is able to offer more stabilization. This phenomenon is not observed for the *meta* position.

Another example:



ETHERS

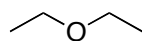
An ether is a substance that has two organic groups bonded to the same oxygen atom, R-O-R', where R and R' can be the same or different, but cannot be carbonyl (C=O), or H directly attached. The organic groups may be alkyl, aryl, or vinylic, and an ether can either be an open chain or a ring. Perhaps the most well-known ether is diethyl ether, a familiar substance that has been used medically as an anesthetic, and is used industrially as a solvent.



diethyl ether

Naming Ethers

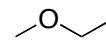
Two systems for naming ethers are allowed by IUPAC rules. Simple ethers with no functional groups are named by identifying the two organic substituents and adding the word *ether* as in the below examples.



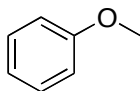
diethyl ether
or ethyl ether
or ether



dimethyl ether
or methyl ether



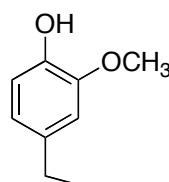
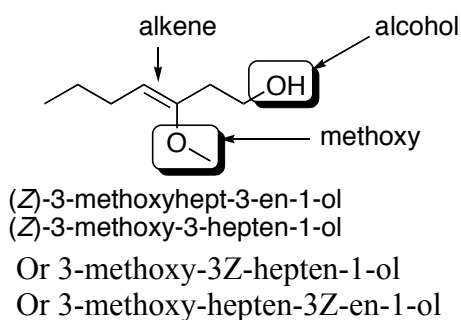
ethyl methyl ether



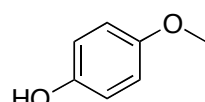
anisole
methyl phenyl ether

If other functional groups are present, the ether part is considered to be an alkoxy substituent (-OR).

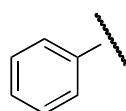
For example, the parent name for the below structure is an alcohol.



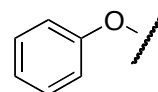
Cockroach sex pheromone
2-methoxy-4-ethylphenol
4-ethyl-2-methoxyphenol



4-methoxyphenol
methyl *p*-hydroxyphenyl ether



phenyl group

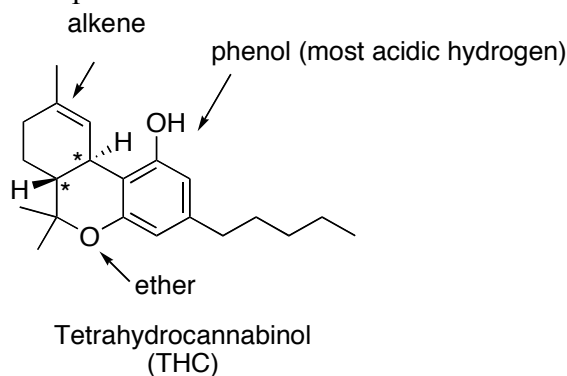


phenoxy group

Ethers: Properties

1. Intermediate polarity - usually have dipoles & can accept hydrogen bonds
2. Not miscible with water - very slight solubility
3. Good solvents for many organic compounds
4. Less dense than water $\rho < 1.0$ - floats on water
5. Usually chemically unreactive - inert to base or weak acid - can react with very strong acid

Example: THC



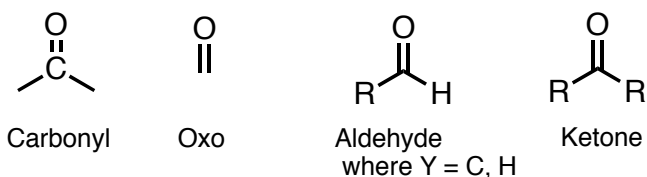
$\text{pK}_a = \sim 10$ like phenol

* = two stereogenic centers

You should be able to identify different functional groups in a large molecule like THC, and be able to find stereogenic centers and identify the configurations. If treated with Br_2 , which double bond will react? *Answer:* Top one (The non-aromatic alkene).

Aldehydes and Ketones: Nomenclature

A carbonyl group has a pi (π) bond between carbon and an oxygen atom. An oxo group is any atom with a double bond to oxygen. Compounds in which there is a carbonyl group are divided into different functional group classes depending on the other groups that are bonded to the carbon atom of the carbonyl group. In aldehydes, the carbonyl group is bonded to at least one hydrogen. In ketones, the carbonyl is bonded to two carbon atoms.



The carbon atom of the carbonyl group is bonded to three other groups, all in one plane, and therefore is trigonal planar. The bond angles between all the groups are approximately 120° and the carbon atom of the carbonyl group is sp^2 hybridized

Aldehyde Nomenclature

Aldehydes are systematically named by changing the ending of the parent alkane and replacing it with *-al*. The numbering of the parent hydrocarbon chain is such that it makes the aldehyde the first carbon of the chain. Other substituents are named using prefixes and numbered to indicate their positions relative to the aldehyde group. For complex examples, the aldehyde functionality can also be called a formyl group.

Aldehydes take higher priority in naming over ketones, alcohols, ethers, amines, alkenes, alkyl halides.



formyl group

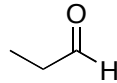
Some common simple aldehydes are given below along with their systematic names.



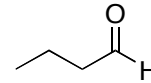
methanal
or formaldehyde



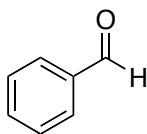
ethanal
or acetaldehyde



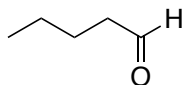
propanal
or propionaldehyde



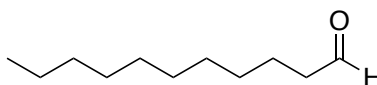
butanal
or butyraldehyde



Benzaldehyde

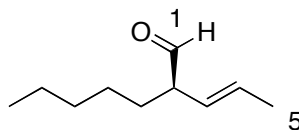


Pentanal
or Valeraldehyde



Undecanal (a sperm attractant)

An example of naming aldehydes is given with the below structure:



(2R,3E)-2-pentylpent-3-en-1-al

Find the parent name of the longest, most functionalized chain. In this case it is 5 carbons long and therefore is a pentane.

There is a trans double bond present in the molecule at position 3. You then drop the *-ane* ending, replacing it with *-ene* to give pent-3-ene.

Since the molecule is an aldehyde, you then drop the *-e* ending, replacing it with *-al* for the name to become pent-3-en-1-al.

There is also a pentyl group at position 2, making the molecule 2-pentylpent-3-en-1-al.

There is also stereochemistry to take into account. The double bond is in the trans geometry and the aldehyde group is in the R configuration. Putting the overall name together gives (2R,3E)-2-pentylpent-3-en-1-al.