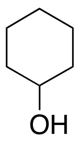
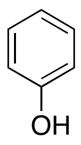
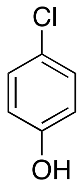
Acidity of alcohols continued …



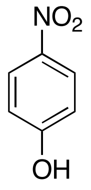
cyclohexanol
$pK_a = 18$



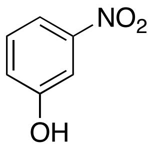
phenol
$pK_a = 10$



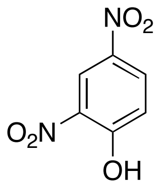
4-chlorophenol
$pK_a = 9.3$



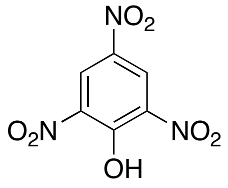
4-nitrophenol
$pK_a = 7$



3-nitrophenol
$pK_a = 9.3$

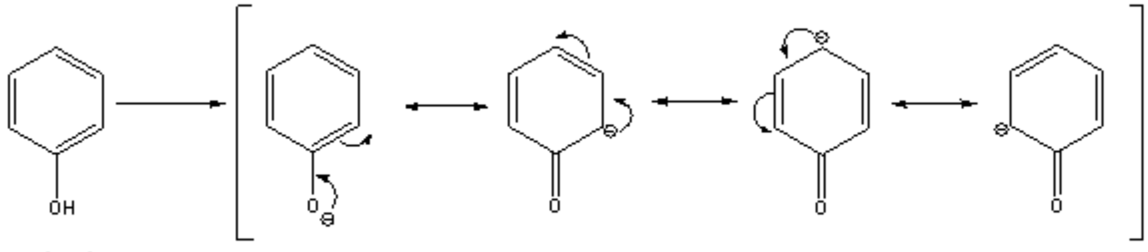


2,4-dinitrophenol
$pK_a = 4.5$



2,4,6-trinitrophenol
picric acid
$pK_a = 0.5$

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



phenol

resonance forms of phenoxide anion

Phenol has a pK_a value of 10 (given this information, you should immediately recognize that it is more much 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^+) ?

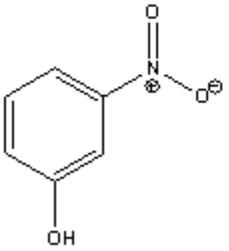
Answer: It lies far to the left (not ionized). Even though phenol is 10^6 more acidic than water, its pK_a of 10 tells you that the acidity constant is 10^{-10} or that only one part in 10^{10} is ionized, the rest exists as phenol with H attached to oxygen.

Example: Chlorophenol (Above)

Is the anion more or less stabilized compared to phenol?

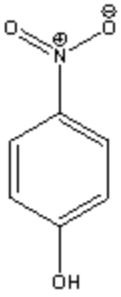
Answer: more stabilized. The chlorine atom is electron withdrawing, and stabilizes the negative charge at the *para* position through the inductive withdrawing effect. However, it also has a weak resonance donating effect. The inductive effect of chlorine wins over resonance effect in this case (contrast this with electrophilic aromatic substitution where the resonance donating effect wins out against the inductive effect).

Example:



m-nitrophenol

VS

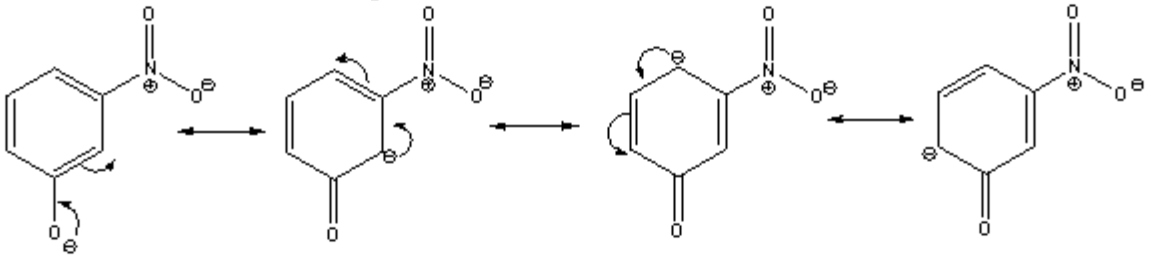


p-nitrophenol

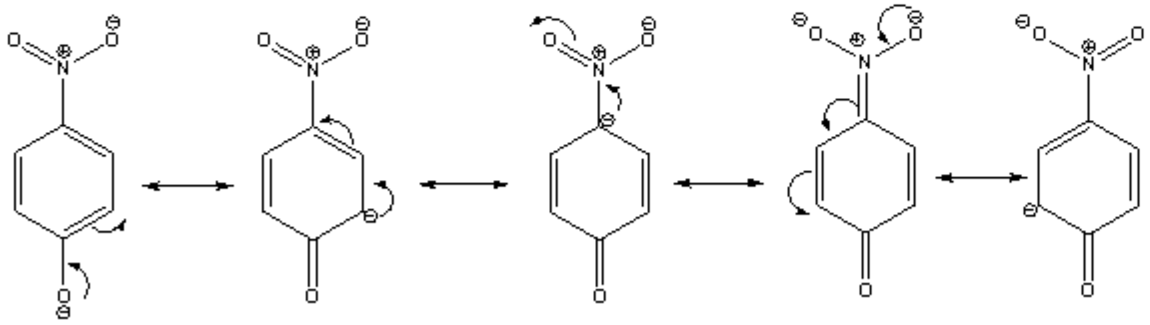
m-nitrophenol has a pK_a value of 9.3, whereas the *p*-nitrophenol has pK_a value is 7.2.

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:

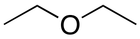


The nitro group offers an additional resonance form for *p*-nitrophenol that is not possible for *m*-nitrophenol (we are able to drive electrons all the way up to the nitro group for the *para*- substituted nitrophenol). Since there is one more reasonable resonance form the *p*-nitrophenol pK_a 7.2 is 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.

Ethers

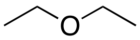
An ether is a substance that has two organic groups bonded to the same oxygen atom, R-O-R', where R and R' can be the same or different, but cannot be carbonyl (C=O) directly attached. The organic groups may be alkyl, aryl, or vinylic, and the oxygen atom can either be an open chain or a ring. Perhaps 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.



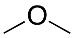
diethyl ether

Naming Ethers

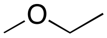
Two systems for naming ethers are allowed by IUPAC rules. Simple ethers with no functional groups are named by identifying the two organic substituents and adding the word *ether* as in the below examples.



diethyl ether
or ethyl ether
or ether



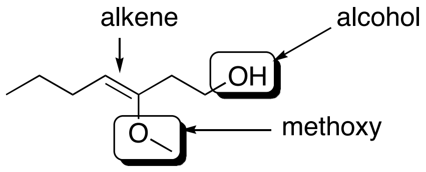
dimethyl ether
or methyl ether



ethyl methyl ether

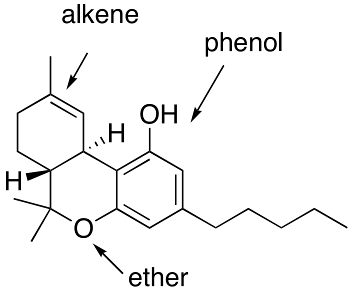
If other functional groups are present, the ether part is considered to be an alkoxy substituent.

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



(*Z*)-3-methoxyhept-3-en-1-ol
(*Z*)-3-methoxy-3-hepten-1-ol

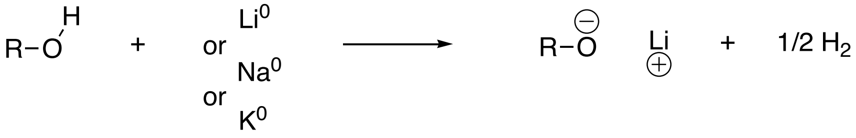
Example:



Tetrahydrocannabinol
(THC)

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

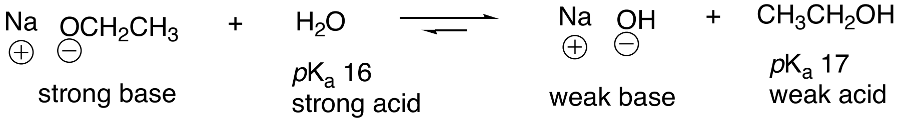
Reactions of R-OH



$$R{-}O{-}H \;+\; \begin{matrix} Li^0 \\ \text{or} \\ Na^0 \\ \text{or} \\ K^0 \end{matrix} \;\longrightarrow\; R{-}O^{\ominus}\;\; Li^{\oplus} \;+\; 1/2\ H_2$$

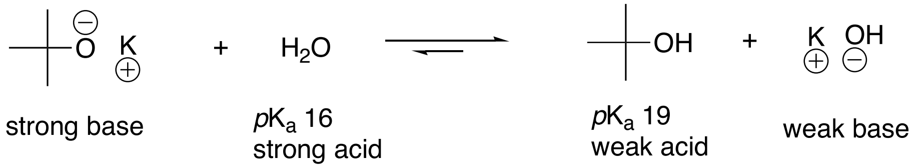
When R = H (water), DEMO on the Na and K metal.

Example:

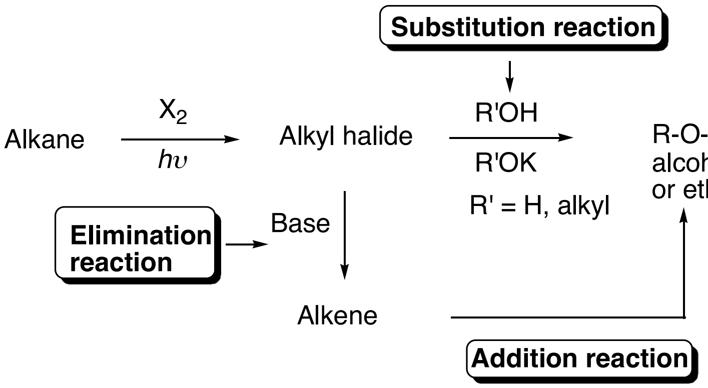


$$Na^{\oplus}\ {}^{\ominus}OCH_2CH_3 \;+\; H_2O \;\rightleftharpoons\; Na^{\oplus}\ {}^{\ominus}OH \;+\; CH_3CH_2OH$$

Example:



Prepare alcohols or ethers from alkanes



Example: