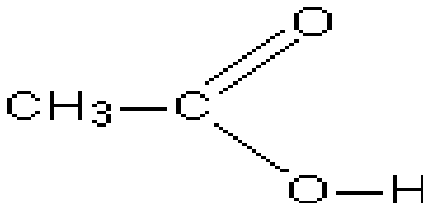
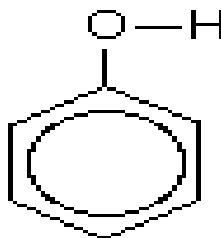


Structural Effects on Acidity

Acidity is associated not only with the tendency of compound to yield hydrogen in H_2O but also to accept an electron pair to form a covalent bond.

The strengths of weak acids are measured on the *pK_a* scale. The smaller the number on this scale, the stronger the acid is.

		pK_a
ethanoic acid		4.76
phenol		10.00
ethanol	$\text{CH}_3\text{—CH}_2\text{—O—H}$	about 16

Variations in acid strengths between different carboxylic acids

	pK_a
HCOOH	3.75
CH_3COOH	4.76
$\text{CH}_3\text{CH}_2\text{COOH}$	4.87
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	4.82

- **The less the charge is delocalized, the less stable the ion, and the weaker the acid.**
- **Alkyl groups have a tendency to "push" electrons away from themselves. That means that there will be a small amount of extra negative charge built up on the -COO- group. Any build-up of charge will make the ion less stable, and more attractive to hydrogen ions.**

Attachment of electronegative atoms like chlorine to the chain.

	pK_a
CH ₃ COOH	4.76
CH ₂ ClCOOH	2.86
CHCl ₂ COOH	1.29
CCl ₃ COOH	0.65

Attachment of different halogen atoms

	pK_a
CH ₂ FCOOH	2.66
CH ₂ ClCOOH	2.86
CH ₂ BrCOOH	2.90
CH ₂ ICOOH	3.17

Attachment of halogen to different C position.

	pK_a
CH₃CH₂CH₂COOH	4.82
CH₃CH₂CHClCOOH	2.84
CH₃CHClCH₂COOH	4.06
CH₂ClCH₂CH₂COOH	4.52

- **The chlorine is effective at withdrawing charge when it is next-door to the -COO- group, and much less so as it gets even one carbon further away.**

General Rule

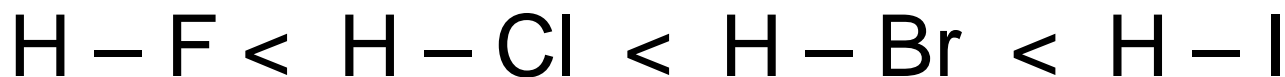
1. Acidity increases as the electronegativity increases

Example:



2. Within the Family, acidity increases as the size increases

Example:

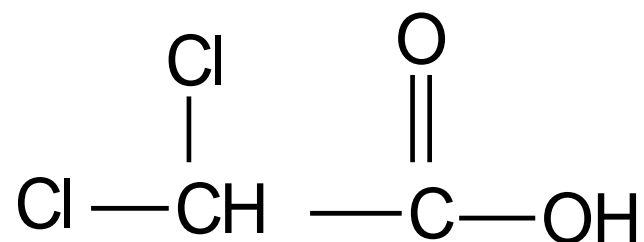
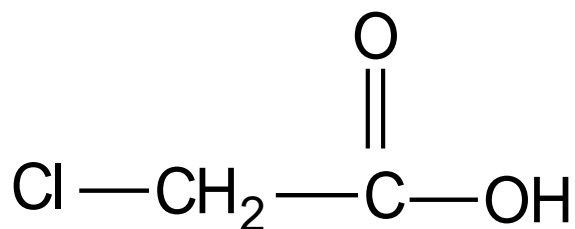


3. The acidity of the H of the carbonyl group is attributed to the electron attracting inductive effect of O and also the pi electron delocalization.

Example:

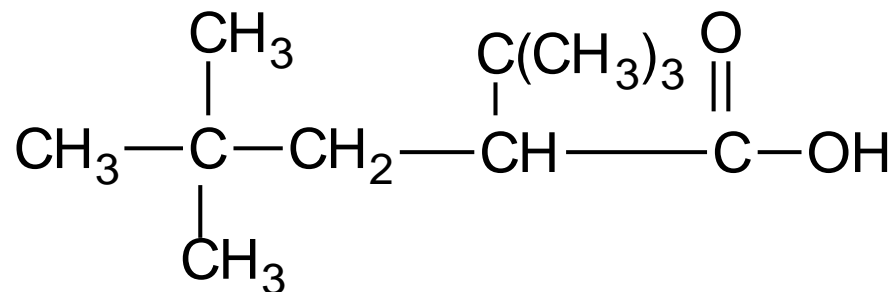
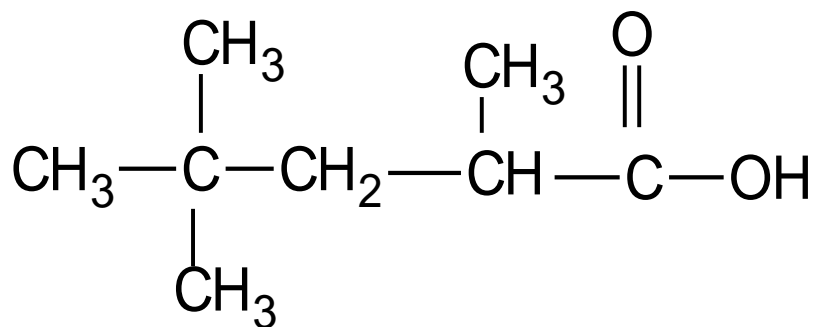


As the size of the R group increases the electron repelling effect increases.



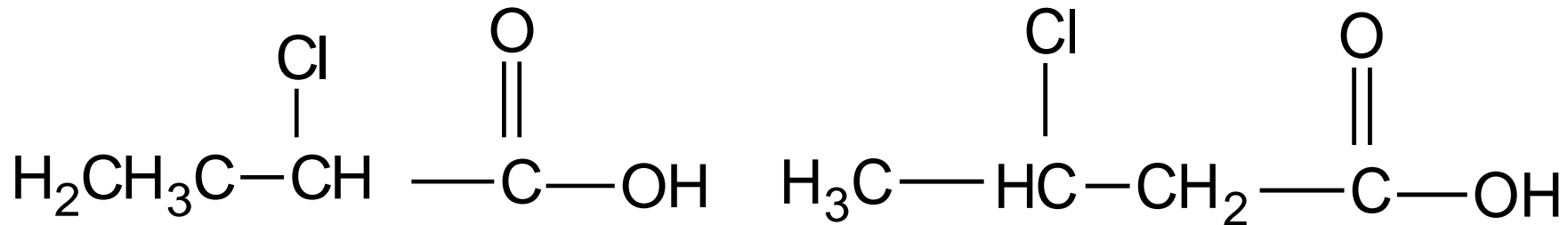
More acidic

Electron inductive effect of the Cl atom increases the positivity of the carbonyl C enhancing the delocalization of the lone pair from O. This will enhance the removal of H from the carboxyl group.



More acidic

Accumulation of the bulky group adjacent to the carbonyl function of aliphatic acid has pronounced acid-weakens in effect. These acids would be subject to steric inhibition of the close approach of solvent molecules which can promote ionization of the hydrogen.



More acidic

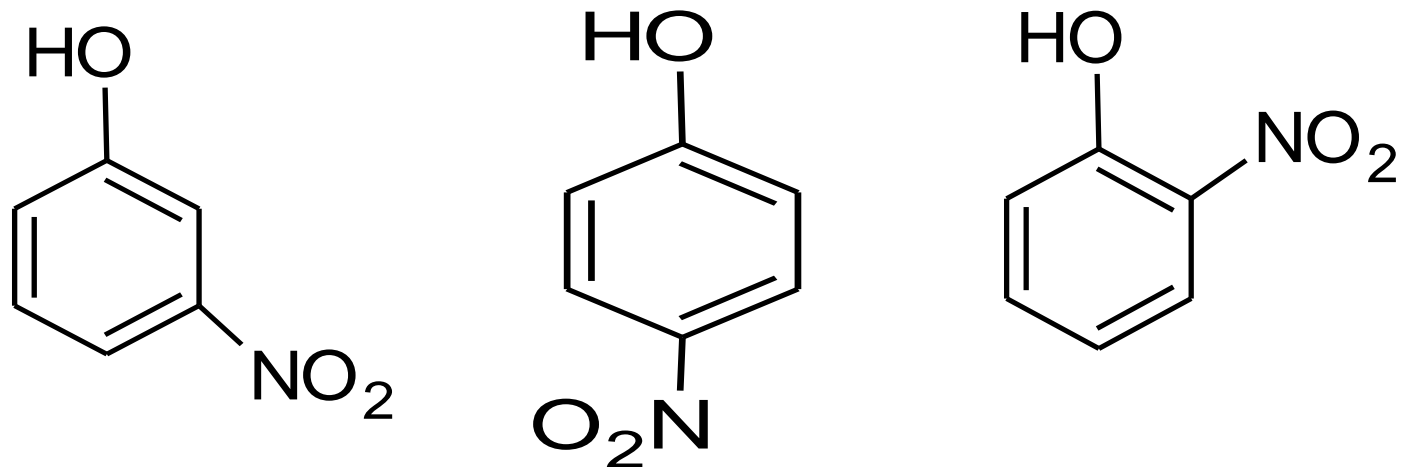
Electron attracting inductive effect of Cl is stronger at the α position, thus inductive effect decreases with distance.

4. Alcohols are weaker acids than phenol because the OH bond in phenol is greatly weakened as a result of π electron delocalization towards the ring. In alcohol the weakening of the OH bond is only due to the electron attracting inductive effect of O.

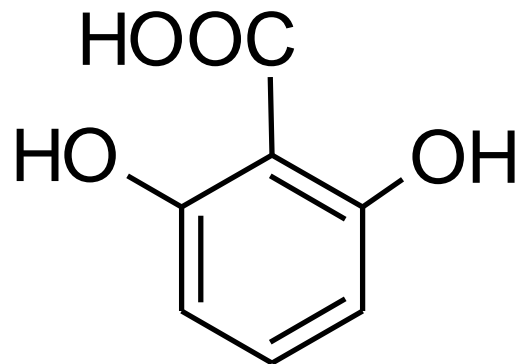
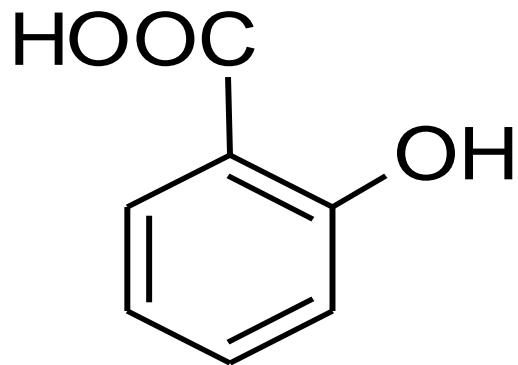
Example:

	ka	
CH_3NO_2	6.1×10^{-11}	
$\text{CH}_3\text{CH}_2\text{NO}_2$	2.5×10^{-11}	3 C-H
$\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{NO}_2$	2.4×10^{-11}	6 C-H

The acidity of the α H is a result of the influence of the nitro group and electron attracting inductive effect.



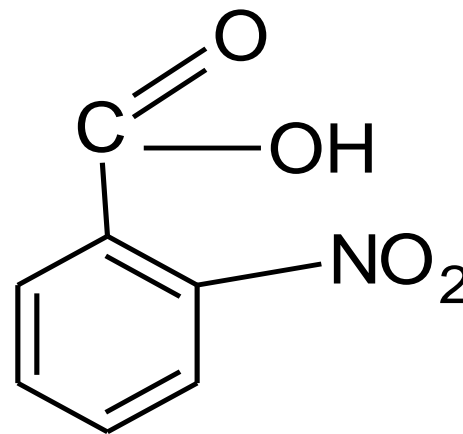
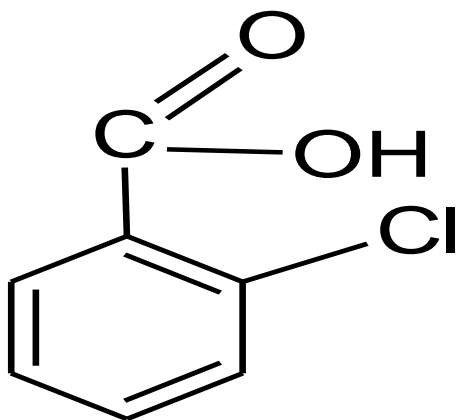
Contribution due to intramolecular H-bonding is not significant in the o- nitrophenol, thus no apparent differences in k_a when nitro group is placed in the o or p position. The greater acidity of the o and p nitrophenols as compared with the meta is attributed to the stronger effect of pi electron delocalization than inductive effect in promoting ionization of H. The meta group is in a position to exercise its inductive effect only. Phenols are not sensitive to steric effect unlike acids.



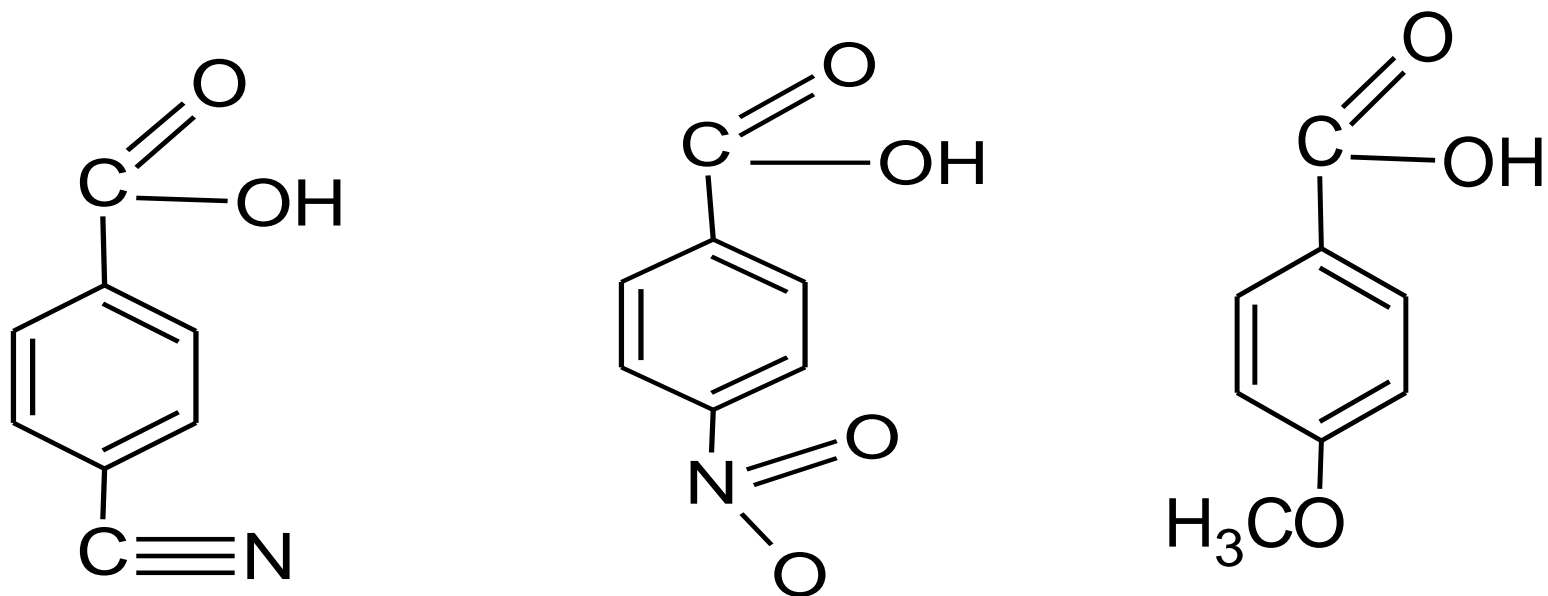
Salicylic acid(2-hydroxybenzoic acid) vs 2,6- dihydroxybenzoic acid

The acidity of 2,6-dihydroxybenzoic acid is greater than that of salicylic acid because of intramolecular H-bonding on both sides of the carboxylate group.

- Steric effect, H-bonding and pi electron delocalization in addition to inductive effects have been associated with the differences in acidic strength of benzoic acid and substituted benzoic acids.



o - nitrobenzoic acid is more acidic because polar effect is considered in addition to steric effect. N is positively charge thus reduces electron density of the carbonyl C and will enhance electron delocalization away from the OH weakening the OH bond.



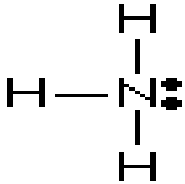
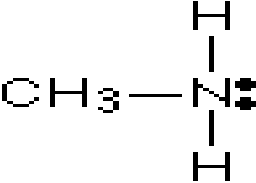
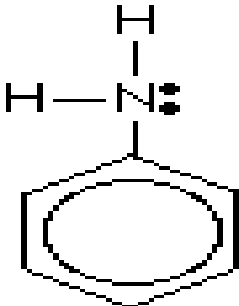
p-cyanobenzoic acid and p-nitrobenzoic acid are more acidic than p-methoxybenzoic acid. p-nitrobenzoic acid is most acidic because of excess positive charge, while cyano is due orbital negativity. p-methoxybenzoic acid is less acidic because they are increasing the e-density of ring

Structural Effects on Basicity

Basicity - is measured in the degree of availability of lone pair for conjugation with acids.

- "a substance which combines with hydrogen ions (protons)".



		pK_b
ammonia		4.75
methylamine		3.36
phenylamine		9.38

methylamine is a stronger base, whereas phenylamine is very much weaker.

General Rule

- 1. All aliphatic primary amines are stronger bases than ammonia.**

For example

pK_b



3.36

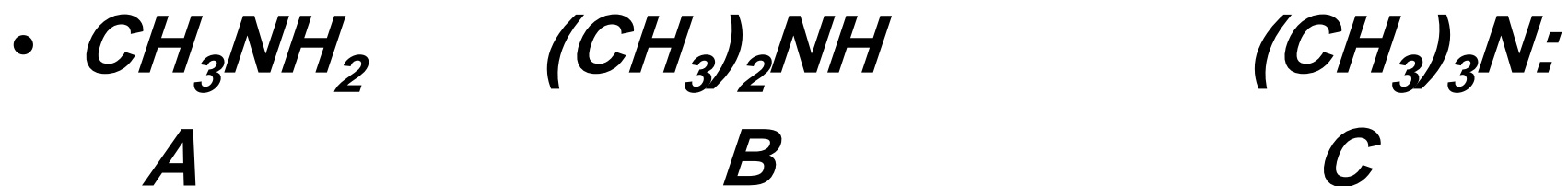


3.27



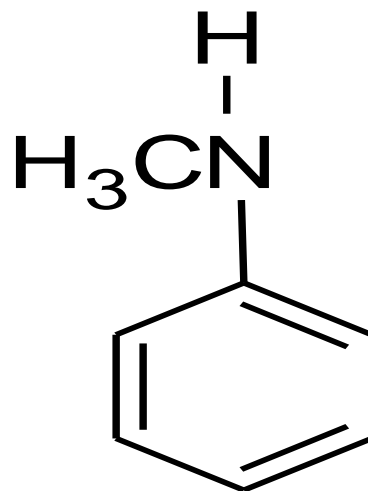
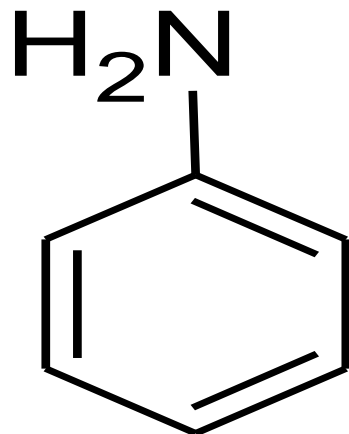
3.16

3. Any group that will donate electron will increase basicity and group which will withdraw electron will decrease basicity.

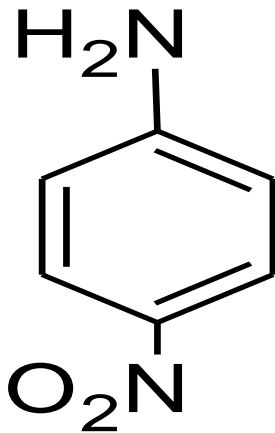
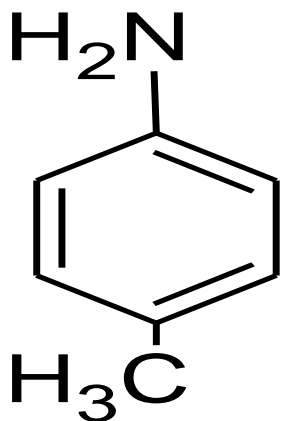


If the reference acid is H^+ then basicity is $\text{C} > \text{B} > \text{A}$ polar effect

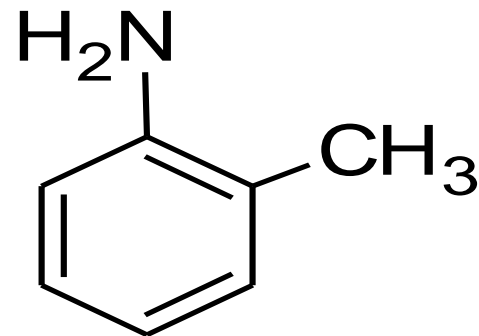
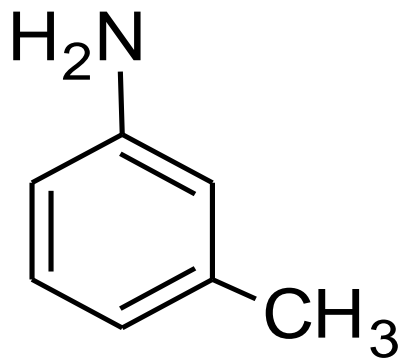
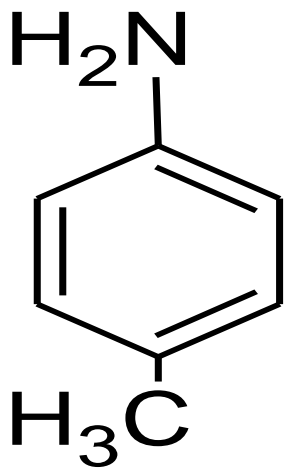
Aliphatic amines are more basic than aromatic amines due to delocalization of lone pair towards the ring making it less available. Presence of alkyl group on N is base weakening due to pushing effect hastening delocalization of lone pair towards the ring.



Presence of electron withdrawing group on aniline decreases the availability of lone pair because of their tendency to withdraw electron from the ring thereby hastening the delocalization of lone pair on N towards the ring

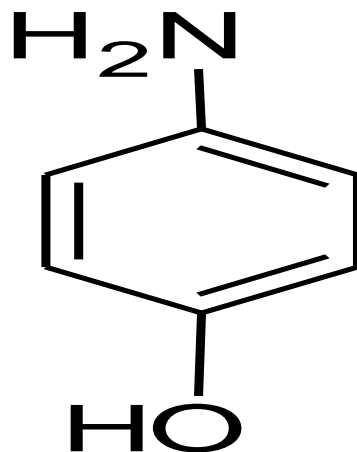
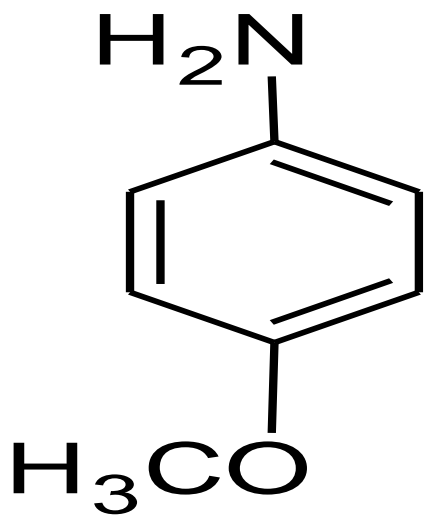


- Presence of electron repelling group has base strengthening effect especially at the para position due to pi electron delocalization or C-H hyperconjugation.***

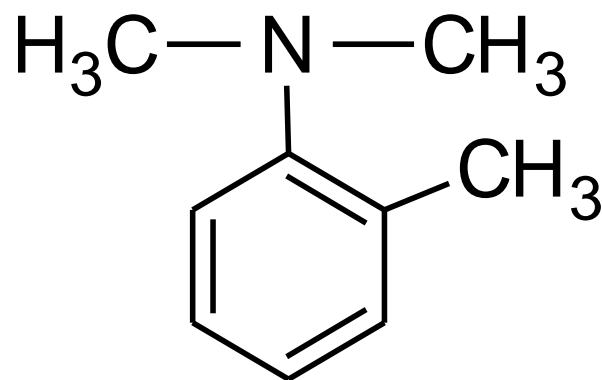
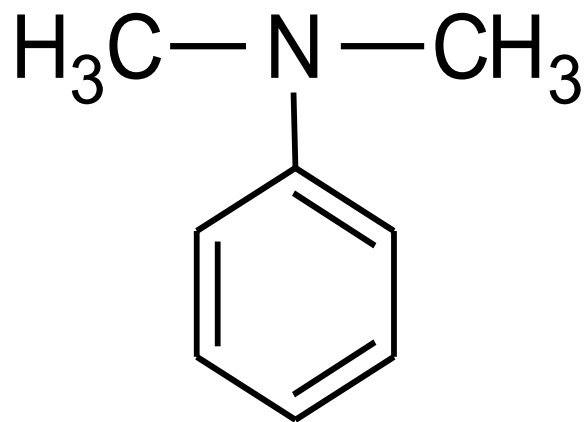


- ***Meta position has weak base strengthening effect due to inductive effect. Ortho position is base weakening due to steric hindrance. Para position exhibits base strengthening effect due to pi electron delocalization towards the N.***

- ***Methoxy and hydroxyl groups are expected to give base-strengthening effects.***



- ***Basicity of some amines is increased by inhibition of resonance or steric inhibition of pi electron delocalization, this decreases the tendency of the lone pair of N to be delocalized.***



- ***Alcohols, esters, ethers, aldehyde, ketones and their sulfur analogs also have available lone pair but these are not as available as that in N hence they are regarded as weak bases.***

Decreasing basicity:

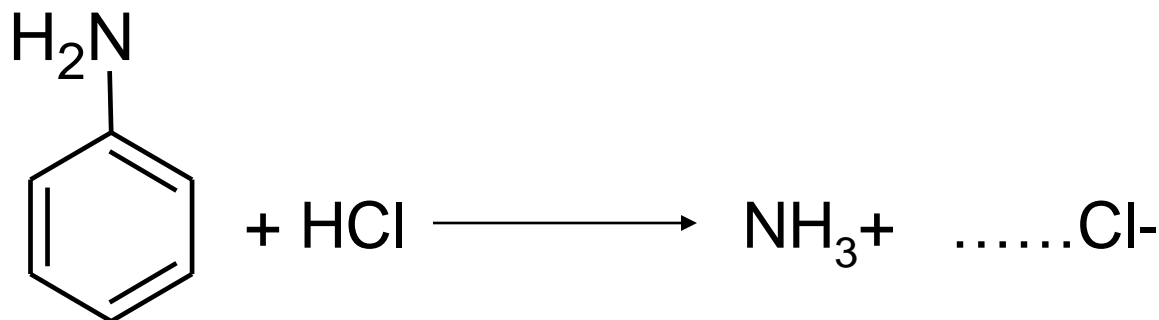
- ***Amines > Ester > ketone > aldehyde > ether > alcohols***

Solubility of Acids and Bases

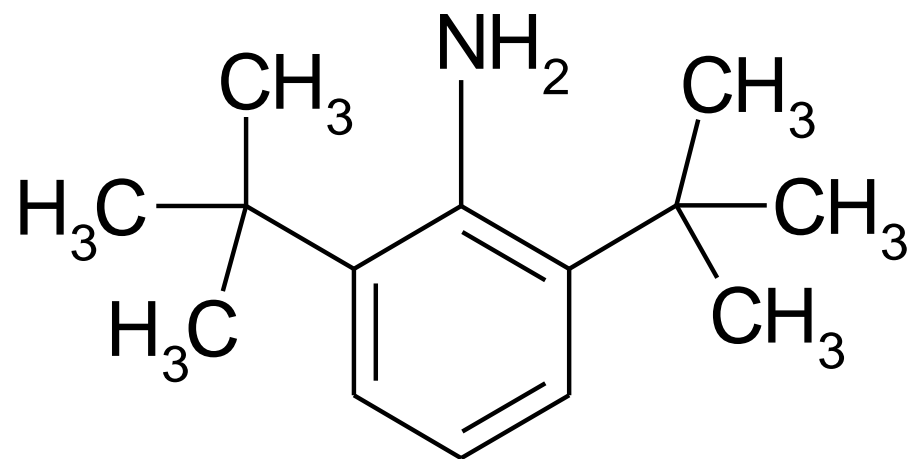
General Rule;

- Strong acids are soluble in strong bases and vice versa.
- Weak bases are soluble in strong acids and vice versa.

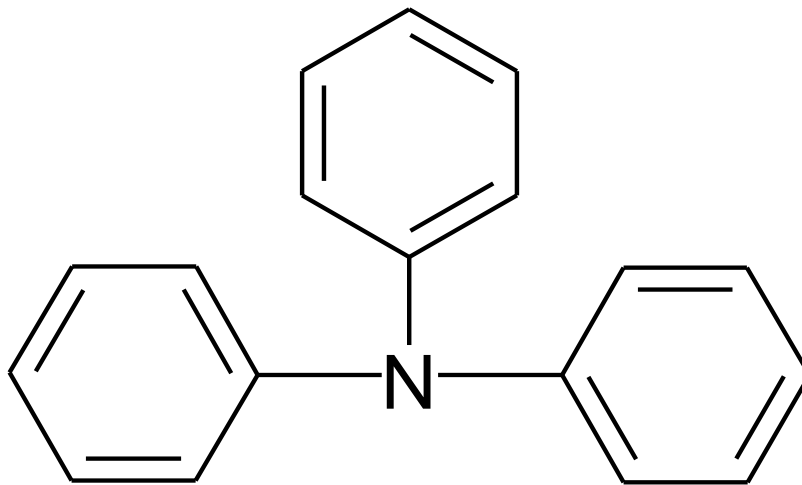
Solubility of amines in dilute HCl is associated with the tendency of the lone pair of electron of N to bond with the proton.



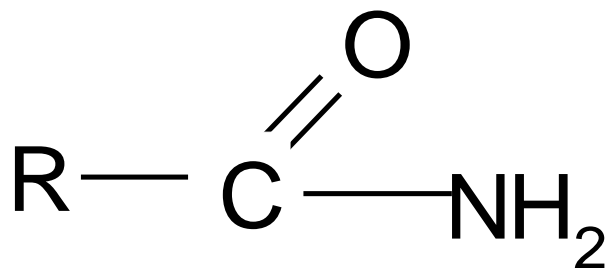
- In general aliphatic amines are soluble in dilute HCl. When alkyl groups are bulky in secondary and tertiary amines, solubility in dilute HCl decreases. This is a consequence of steric inhibition of the approach of the acid to bond with the lone pair or the instability of the salt formed as a result of steric overcrowding.



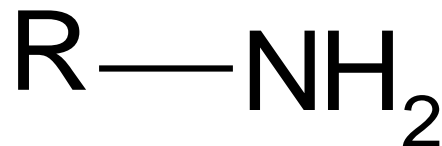
Triphenylamine is not soluble in dilute HCl because of unavailability of the lone pair for coordination with the acid as result of resonance effects or effects due to electron delocalization.



Amides are not soluble in dilute HCl as simple amines because of lesser availability of lone pair of electron of the N of amides compared with simple amines. The lone pair of amides is delocalized towards the carbonyl carbon.

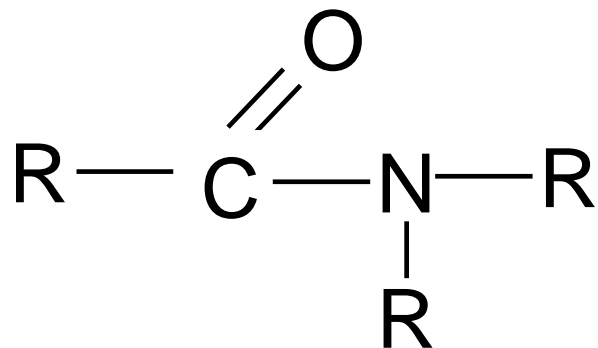


amides

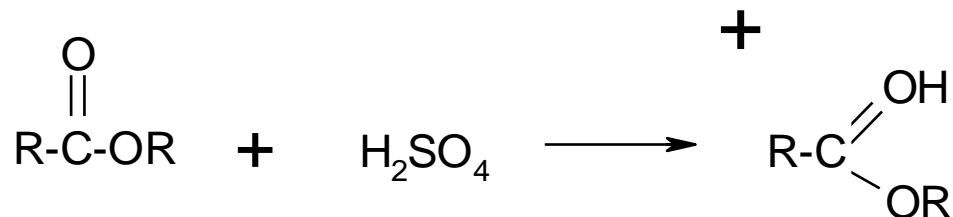
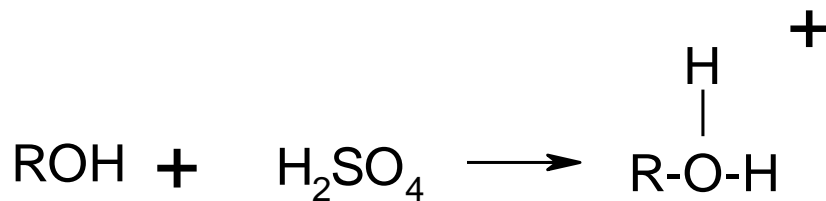
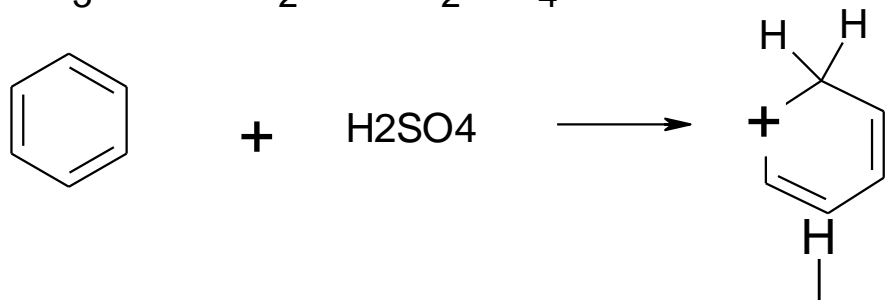


amines

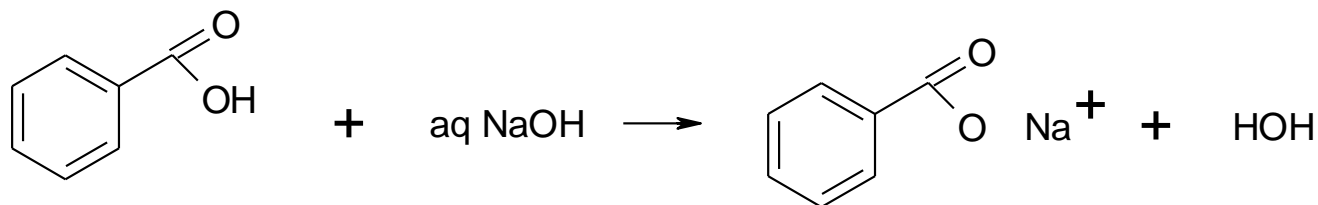
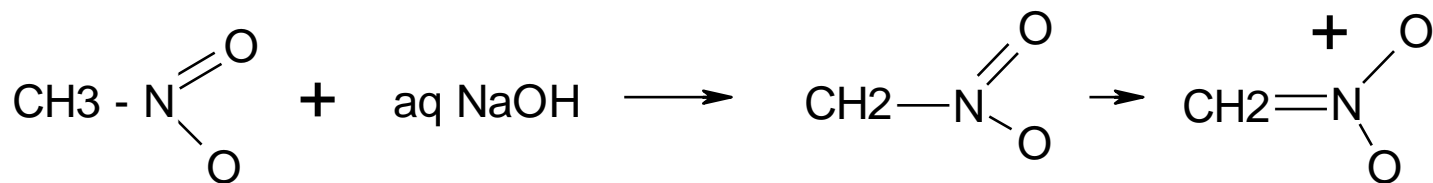
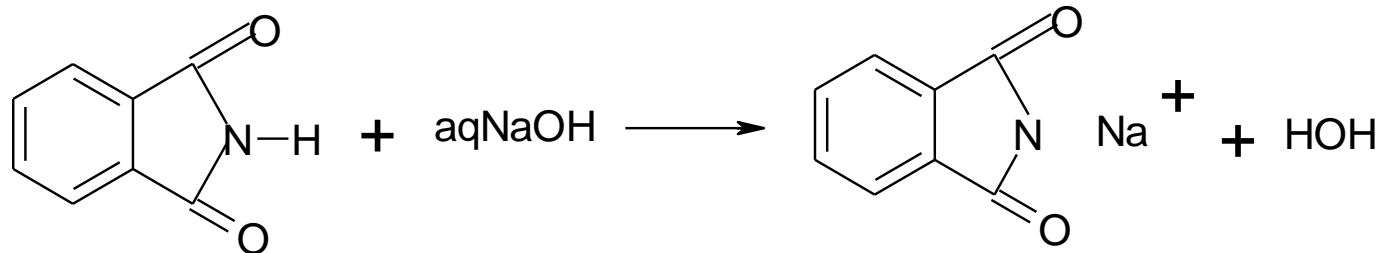
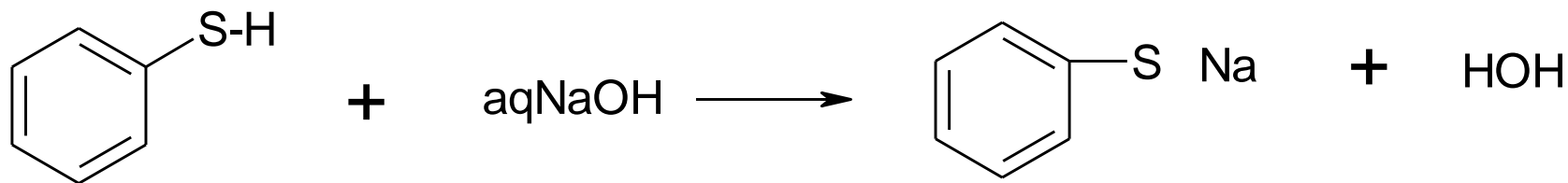
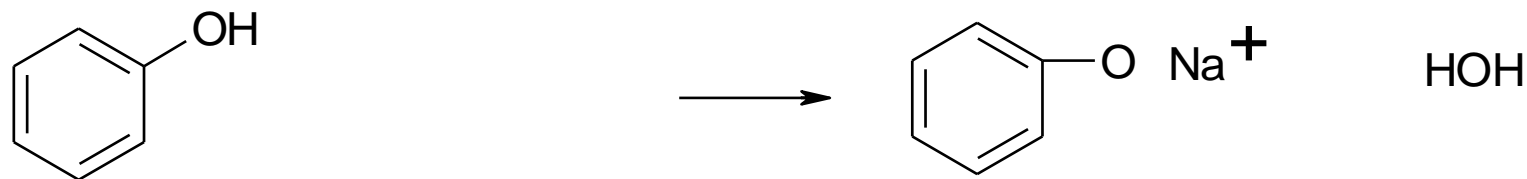
Disubstituted amides, however, in contrast to the simple amides are more soluble in dilute HCl. In these disubstituted amides the alkyl groups increases the availability of the lone pair of electrons on the nitrogen for the acid to coordinate with.



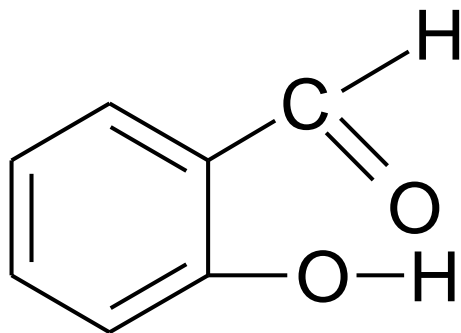
Solubility of unsaturated noncyclic hydrocarbons and some aromatic hydrocarbons in cold concentrated H_2SO_4 is a consequence of the availability of pi electron for coordination with proton.



Solubility of organic compounds in dilute sodium hydroxide is a consequence of the presence of acidic hydrogen.



In chelated phenols, acidic H is tied up as a hydrogen bond, thus insoluble in dilute NaOH.



- Ketones and aldehydes are insoluble in dilute NaOH even though they possess acidic H, because the acidity of H is too weak to allow dissolution in dilute NaOH.
- Solubility of organic compounds in dilute sodium bicarbonate (NaHCO_3) can reflect strength in acidity of these systems. Only carboxylic acid, sulfonic acids, and sulfinic acids are soluble in dilute sodium bicarbonate solution (NaHCO_3).
- Phenols and aliphatic alcohols which are regarded as weak acids do not dissolve in NaHCO_3 , but 2, 4, 6-trinitrophenol is an exception, because the 3 NO_2 increases the acidity of phenol.

- Solubility of chloroform in organic bases such as pyridine and trimethylamine is a consequence of H- bonding.
-
- Solubility of unsaturated noncyclic hydrocarbons and some aromatic hydrocarbons in cold concentrated H_2SO_4 is a consequence of the availability of pi electron for coordination with proton.
-