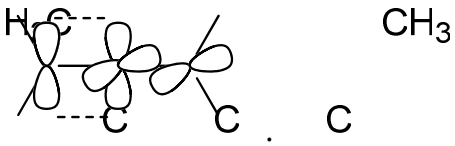
Lesson 3 For Organic Chemistry

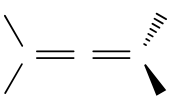
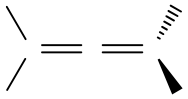
Revision Exercise and Extra Knowledge --- Internal plane of symmetry

Qu: By considering the 3-D structure of the following pair of compounds, state their relationship.

→ Actually, they are a pair of e_____. Note that it is the case in which the compounds have **no** chiral centre, but, they are still **enantiomeric**.

→ Because of the fact that C=C double bond cannot be r_____, the two compounds cannot be made equivalent. Most importantly, you should know that the two pi-bonds should be orthogonal to each other because of the '**sideway overlapping**' nature of pi-bonds : i.e. 

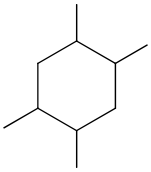
→ In view of the 3-D structures of these two compounds, they can be represented by:

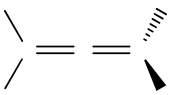

and


respectively. Obviously, they are not the same and they are not superimposable to each other. Hence, they exhibit **enantiomerism**.

→ A simplier way to identify the relationship is to see whether the compound has an internal plane.

→ An **internal plane** is defined as the plane which can **divide** the molecule by two **identical** parts.

→  has _____ internal planes and hence it should be non-enantiomeric.

→ 
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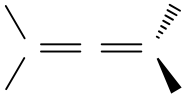
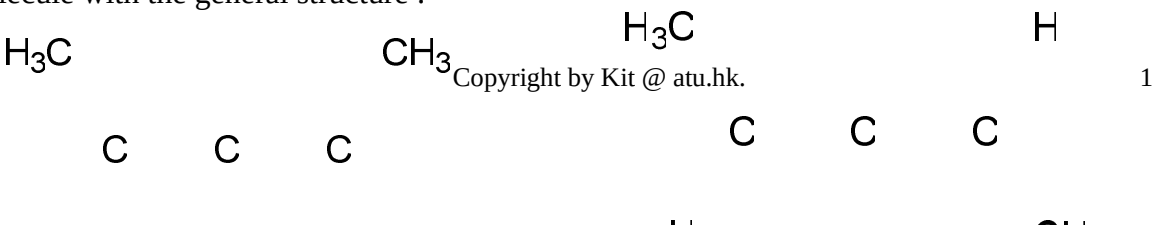

has **no** internal plane and so, they are enantiomeric.

→ A rule can be stated as if there is no internal plane, the molecule is likely to be enantiomeric.

→ As mentioned before, a ___ carbon bonded with ____ different groups is likely to be enantiomeric because there is a **chiral centre**. That can be interpreted as : there is an absence of internal plane for those molecule with the general structure : 



Acidity and Basicity

Before exploring the chemistry of different families of organic compounds, we should be familiar with the type of question about the comparison of acidity or basicity of organic acids or bases. Note that organic compounds like c_____ acids are **acidic** while organic compounds like a_____ are **basic**.

1. Origin of acidity and basicity

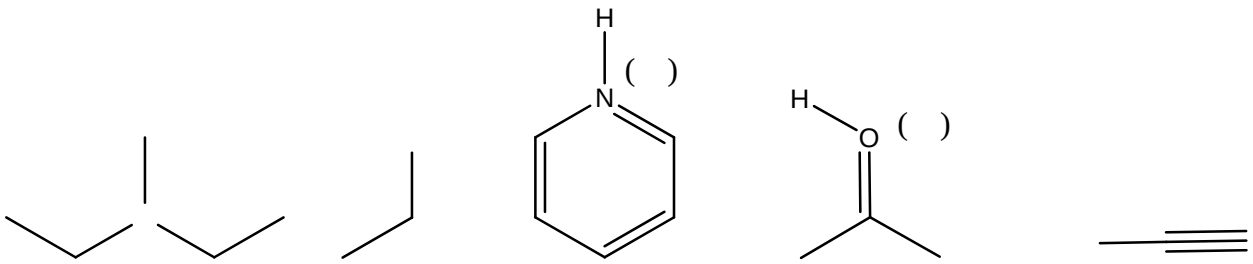
As mentioned before, organic acids are all p_____ donor. They can dissolve in water to give out ___ with the establishment of equilibrium : R---H + H_2O $\rightleftharpoons$ $R^- + H_3O^+$. Basically, carboxylic acids and also lower members of alcohols are good acids.

Meanwhile, organic bases are all proton a_____. They can dissolve in water to give out ___ with the establishment of equilibrium : R + H_2O $\rightleftharpoons$ $R^+ + OH^-$. Bascially, amines are good bases.

Exercise 1 --- Identification of charge

You should be aware that when an organic compound is protonated or deprotonated, it will be charged afterwards. However, you should know the position of the charged atom since an organic compound may be formed by several atoms. In general, you should know that some atoms will bear a **specific charge** when they are carrying several numbers of atoms/groups.

Qu: Please fill in the blank with the correct charge (if any).



→ Hint: We have H_2O, OH^-, H_3O^+, NH_3, NH_2^-, NH_4^+.

2. General method to determine the relative acidity and basicity

First, note that the strength of an acid or a base is just a relative comcept. So, in HKAL, there are many questions asking students to **compare** the acidity or basicity of the given acids or bases.

Remember that the stronger the acid (base) is, the _____ of K_a (K_b) will the acid (base) have. In other words, the stronger the acid (base) is, the _____ of pK_a (pK_b) will the acid (base) have.

A simple rule to compare the acidity or basicity can be stated as :

The stronger the acid (base) is, the more stable the conjugate base (acid) will be.

→ Note that the conjugate species should be in the form of **ion**. If the **charge** on the ion can be **stabilized**, the conjugate species will then have a _____ stability.

3. Acidity

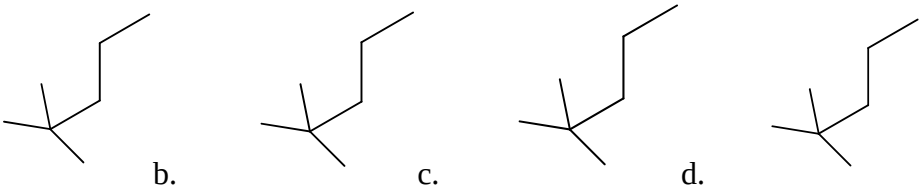
To answer such a kind of 'comparison' question, you should first give a brief **definition** of the term acidity is. In fact, there are two alternative definition of the term acidity.

1. Acidity of a species is a measure of the stability of the conjugate base i____.
2. Acidity of a species is a measure of the ability to d_____ a proton to a base.

Usually, we adopt the **first** definition to anwser question. By thinking of the below effects which will affect the **stability** of the conjugate base ion, you should be able to compare the acidities of the given acids.

Case 1 Inductive effect

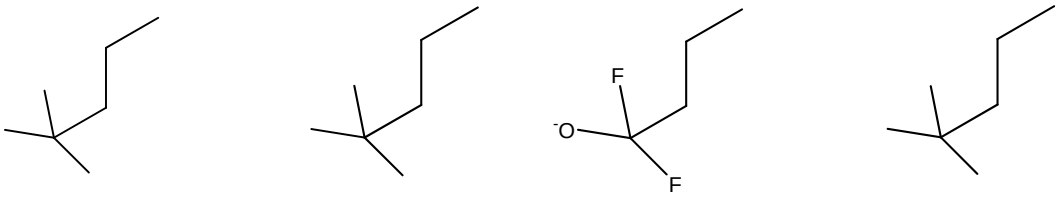
Qu: Please arrange the following acids (alcohols) in the descending order of acidity.



a. b. c. d.

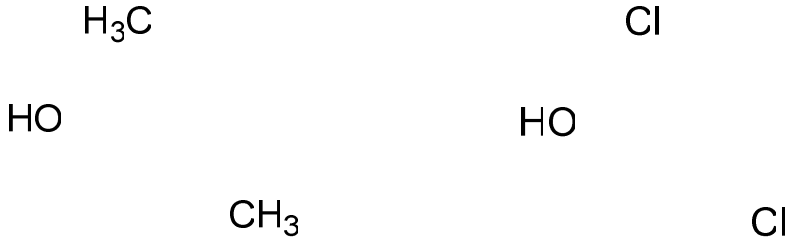
→ The order should be : __> __> __> __.

→ 1st step : Acidity of a species is a measure of the s_____ of the conjugate base **ions**:



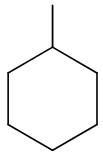
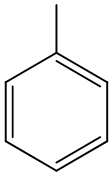
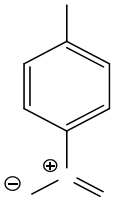
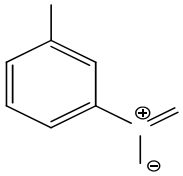
→ Electron-donating group (all alkyl groups) will pose a positive inductive effect on the –ve charge. The conjugate base ion will become **more electron-rich** and hence be **destabilized**. = __ is the weakest.

→ Electron-withdrawing group (all electronegative atoms) will pose a negative inductive effect on the –ve charge. The conjugate base ion will become **less electron-rich** and hence be **stabilized**. Also, note that the electronegativity of halogen d_____ alone the group. = ___ is the strongest.



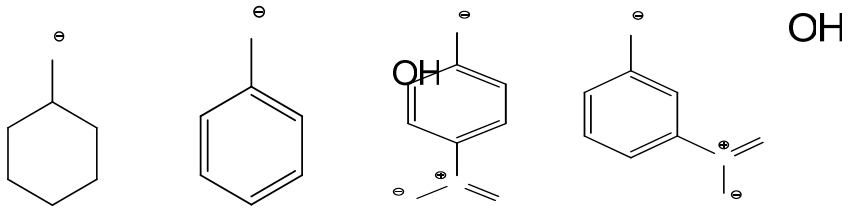
Case 2 Resonance Effect

Qu: Please arrange the following acids (alcohols and phenols) in the descending order of acidity.

a.  b.  c.  d. 

→ The order should be:__> __> __> __.

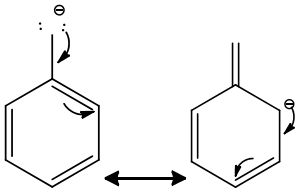
→ Acidity is a measure of the s_____ of the conjugate base i____:

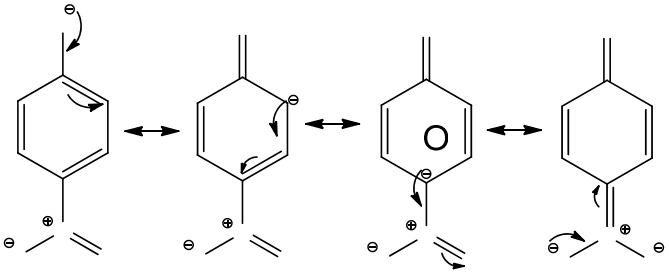


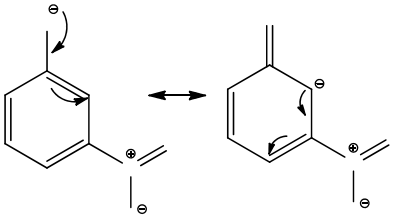
→ Note that the above acids involve the presence of conjugated system (except the species __).

Hence, **resonance effect** should be the major factor which affect the stability of the ions. Remember that :

An ion will be more stable if it has more possible resonance structures.

→ For b:  (three more…)

***→For c:  (three more…)

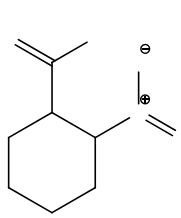
→ For d:  (three more…)

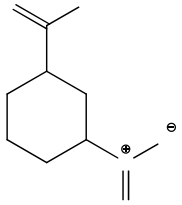
→ Hence, c has the highest number of resonance structure. Its ion is the most stable and hence, ___ is the strongest acid.

→ Note that the **position** of the **nitro group** (-NO_2) is critical for the resonance pathway.

Case 3 Formation of intramolecular hydrogen bond

Qu: Please arrange the following nitro-substituted carboxylic acids in the descending order of acidity.


a)

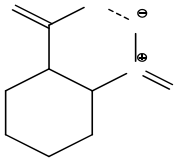

b)

→ The order should be ___> ___.

→ Specially, this time we need to consider the **definition 2** for acidity, that is :

Acidity of a species is a measure of the ability to d_____ a proton to a base.

→ As it can be easily visualized, _____molecular hydrogen bond can be formed within molecule a as :

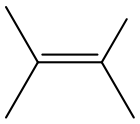


. As a result, the acidic proton on it was bonded **more tightly** and hence, its acidity becomes _____ Since it is more difficult to d_____ a proton to a base. (/ The process become more ____thermic.)

Further Thinking

Qu1: Please arrange the following hydrocarbons in the descending order of acidity. ***


a)


b)


c)

→ The order should be ___> ____> ____.

→ Note that the acidic protons in concern are attaching to carbon atoms with different hybridization states. The states for the carbon atoms on a, b and c are ___, ___, and ____ respectively.

→ By adopting the definition 1 for comparison, it follows that the conjugate ions of c is the most stable because the **sp hybrid orbital** involved has a higher s character (___%) than the others. Hence, the negative charge will be stabilized most.

Qu2 : Given that the **pKa** value of CH_3-OH is 16 while that of **CH_3-SH** is 10. Explain the fact. ***

→ By adopting the definition __, it follows that the proton on CH_3SH is more easily to be d_____. It is because the ____ bond is longer than the _____ bond and hence it is weaker. Thus, the proton on the thiol is more acidic than that on the alcohol.