



GENERAL ORGANIC CHEMISTRY - 4



Objectives

- 1. Resonance or Mesomeric effect**
- 2. Inductive effect**
- 3. Electromeric effect**
- 4. Hydrogen bond**
- 5. Hyper conjugation**
- 6. Steric effect**

Resonance or Mesomerism

1. All the properties of a compound cannot be explained by single structure.
2. Canonical structures or resonance contributing structures—differ in position of electrons.
3. Delocalisation of electrons leads to decrease in potential energy of molecule.



canonical structures of benzene



Resonance hybrid structure of benzene



Resonance or Mesomerism

- 4. Resonance hybrid is more stable than canonical structures.**
- 5. Resonance structures are imaginary.**
- 6. Resonance energy = Actual energy of hybrid – energy of most stable contributing structure.**
- 7. Resonance is measure of stability.**

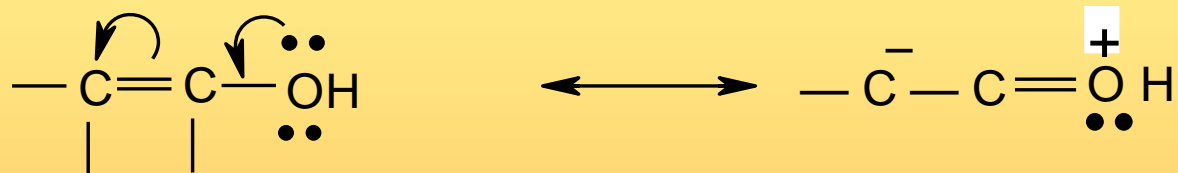


Rules for Drawing Resonance Structure

- 1. The molecule should be planar.**
- 2. It contains an alternating system of single and double bonds (a conjugated system).**
- 3. The relative positions of nuclei should remain unchanged (e.g. tautomerism).**
- 4. The negative charge must preferably lie on the most electronegative atom.**
- 5. The charge needs to be preserved in all the resonating structures.**
- 6. The electrons always move away from a negative charge.**
- 7. Arrows should be drawn to indicate the direction of the movement of electrons.**

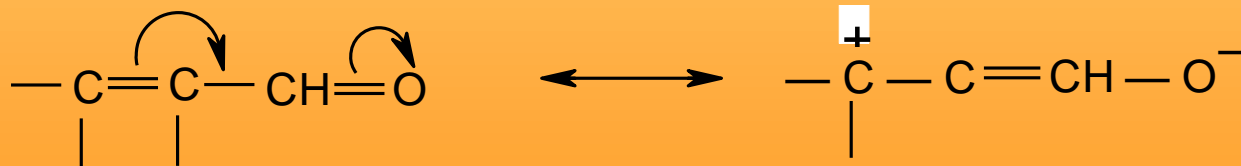
Types of Resonance

+R or +M effect



(+M or +R effect of $-\text{OH}$ group)

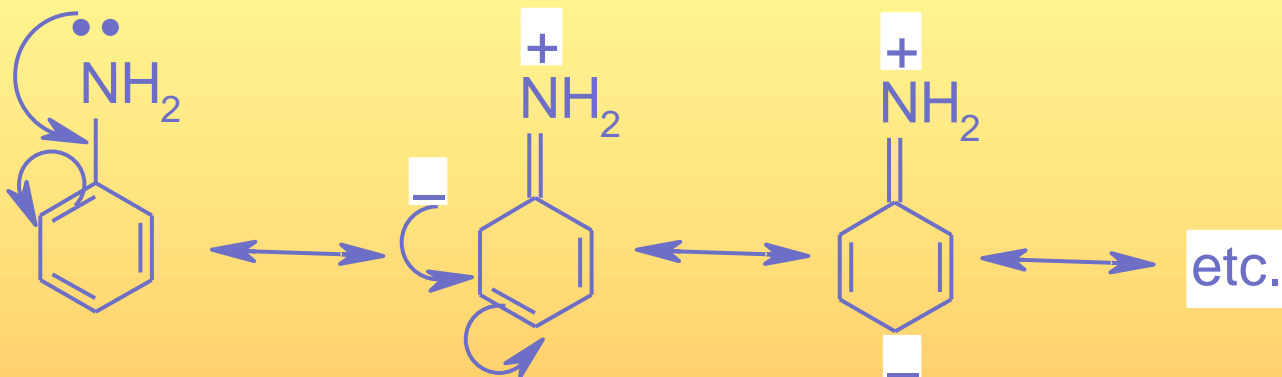
-R or -M effect



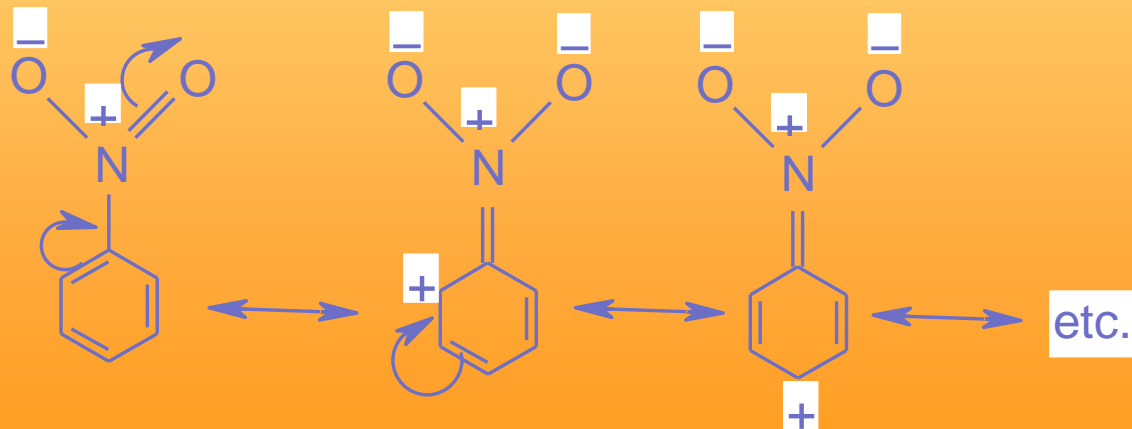
(-R effect of $-\text{CHO}$ group)

Types of Resonance

For substituted benzene



+R effect of $-\text{NH}_2$ group.



-R effect of $-\text{NO}_2$ group.



Inductive Effect

1. Permanent effect in saturated carbon chain compounds.
2. Group attached to carbon chain should have tendency to release or withdraw electrons.

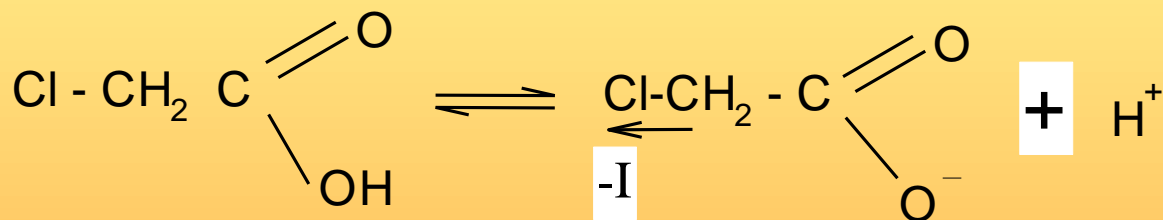
Types of inductive effect

+ I effect effect –electron donating groups
e.g., CH_3 , C_2H_5

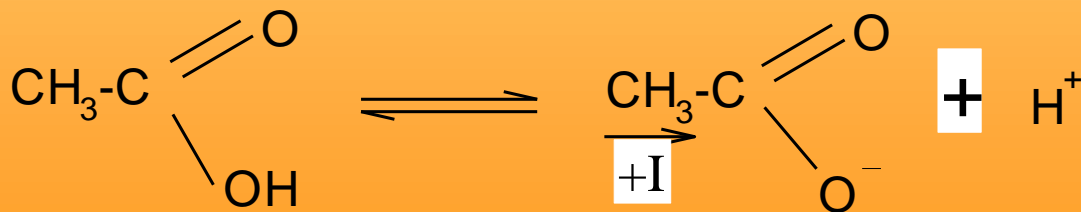
– I effect effect –electron withdrawing groups
e.g., $-\text{NO}_2$, $-\text{CN}$

Features of Inductive Effect

1. Chloroacetic acid is a stronger acid than acetic acid because



$$K_a = 1.4 \times 10^{-3}$$



$$K_a = 1.75 \times 10^{-5}$$

Features of Inductive Effect

2. The larger is the electron-withdrawing effect of a group, the greater is the $-I$ (inductive) effect.



$$K_a \quad 2.5 \times 10^{-3}$$



$$1.3 \times 10^{-3}$$

3. Inductive effect is additive



$$K_a \quad 2.3 \times 10^{-1}$$



$$5.4 \times 10^{-2}$$

Features of Inductive Effect

4. Since this effect is transmitted through a chain it becomes less effective with distance



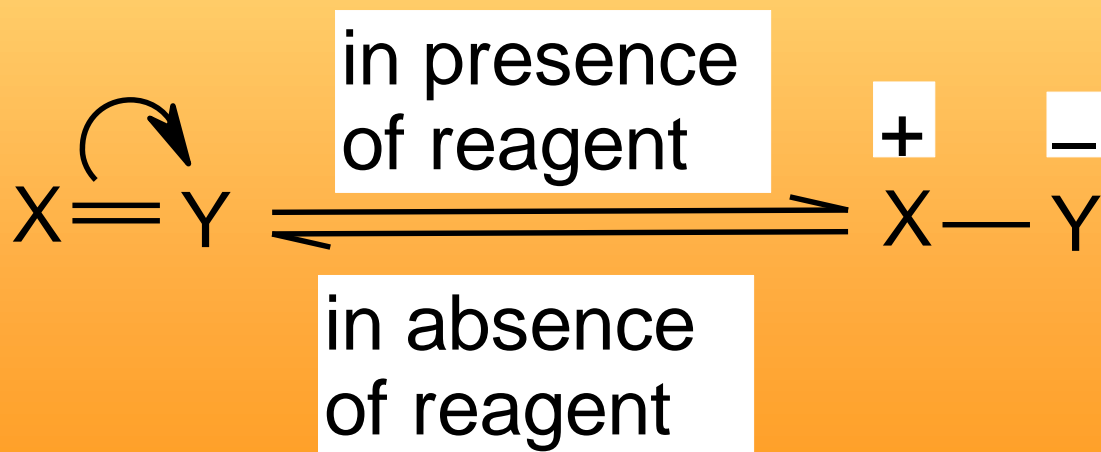
$$K_a \quad 8.32 \times 10^{-4}$$



$$3.02 \times 10^{-5}$$

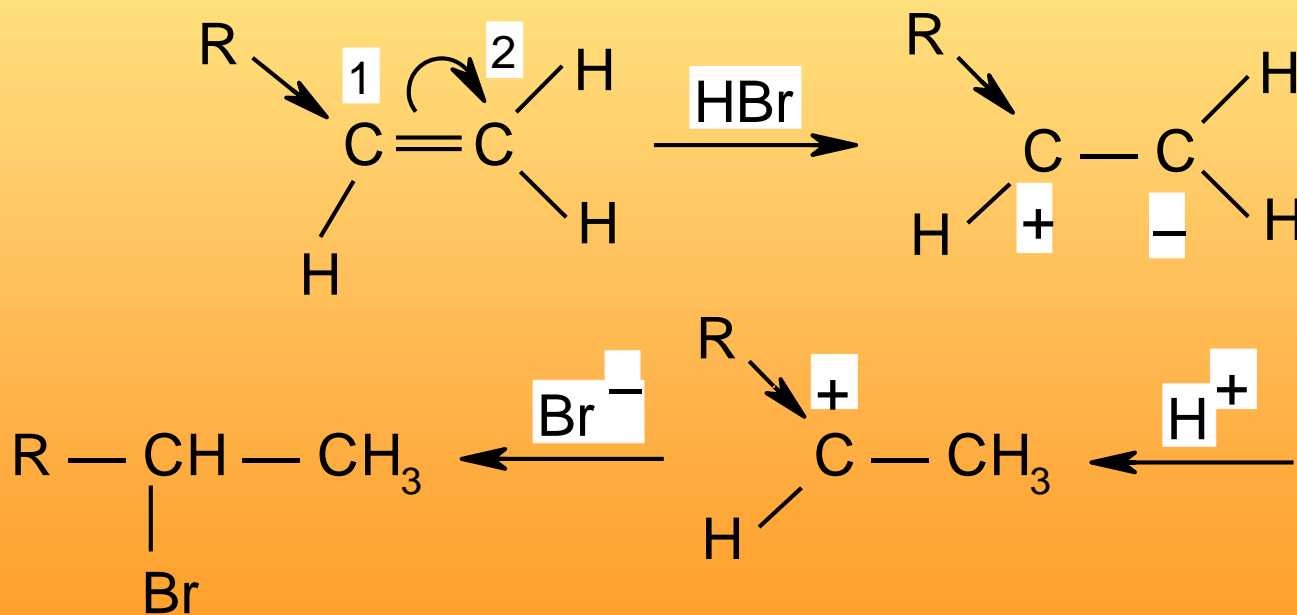
Electromeric Effect

Temporary effect which is observed in presence of reagents involving transfer of electrons in an unsaturated system.



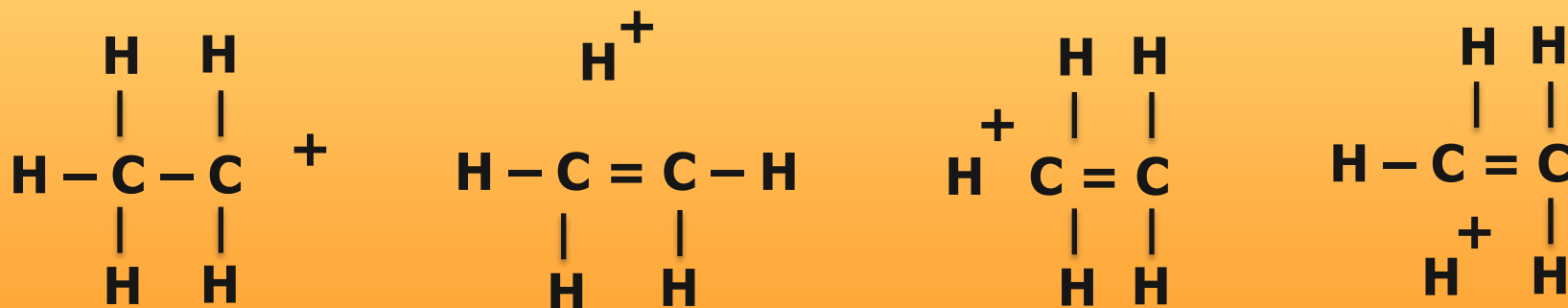
Electromeric Effect

Addition of HBr to an alkene



Hyperconjugation or no bond resonance

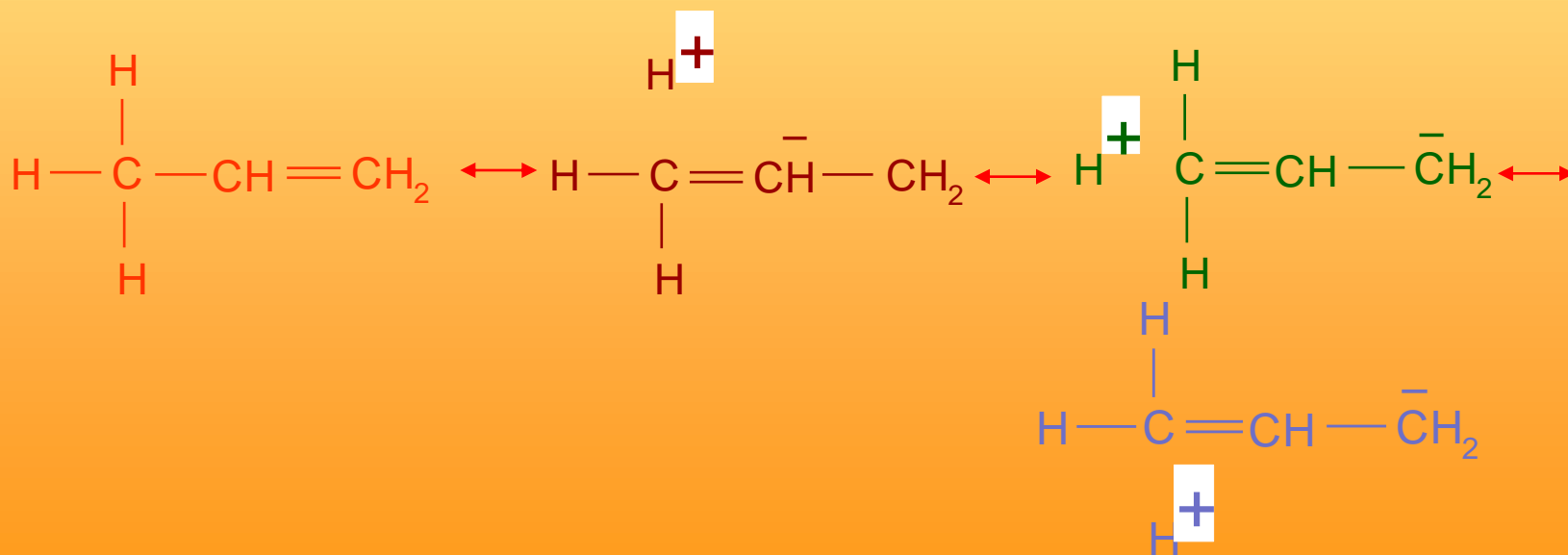
- (a) Involves σ and π bond orbitals
- (b) More the number of hyperconjugative structures, more will be the stability of ion or molecule



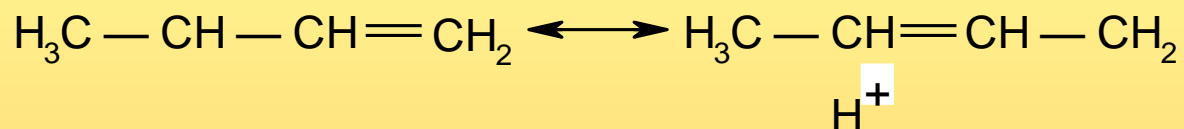
Structure of ethyl carbonium ion

Hyperconjugation or no bond resonance

(c) The number of hyperconjugative structures in an alkene is obtained by the number of C — H bonds attached to the carbon bonded directly to the double bonded carbon atoms.

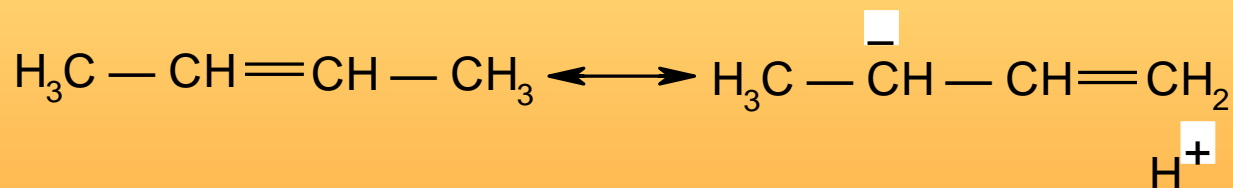


Significance of Hyperconjugation



1-butene

(2 hyperconjugative structures)

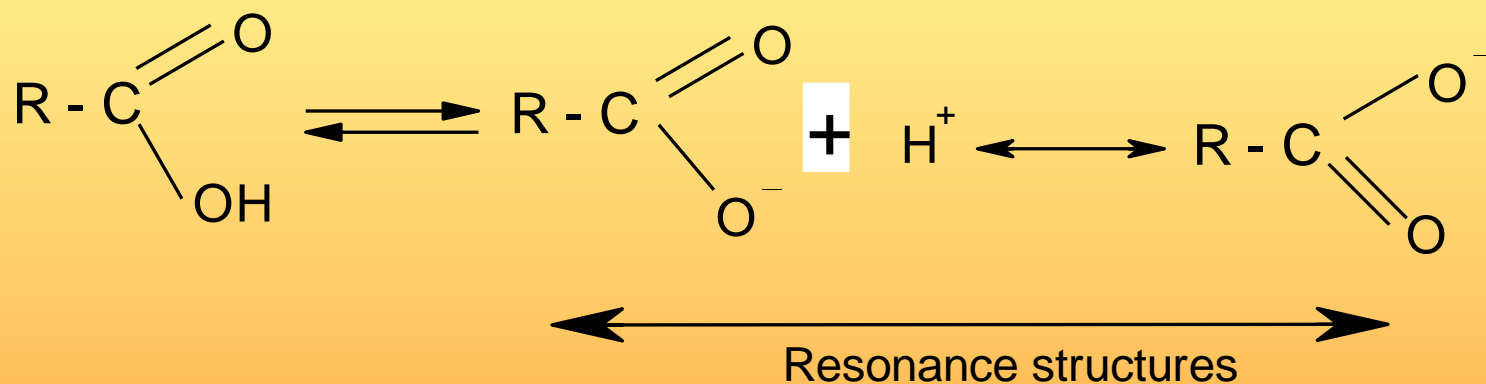


2-butene

(6 hyperconjugative structures)

More stable

Relative strength of organic acids



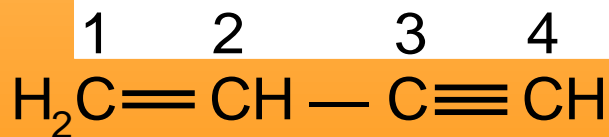
Class exercise 1

The hybridization of carbon atoms C — C single bond in vinylacetylene is

(a) $sp^3 - sp^3$ (b) $sp - sp^2$

(c) $sp^2 - sp$ (d) $sp^3 - sp$

Solution :



Vinylacetylene

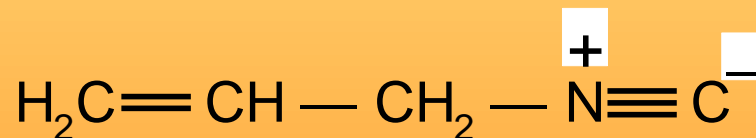
Hence answer is (c).

Class exercise 2

Allyl isocyanide has

- (a) 9 σ bonds and 4 π bonds
- (b) 8 σ bonds and 5 π bonds
- (c) 8 σ bonds, 5 π bonds and 4 non-bonding electrons
- (d) 9 σ bonds, 2 π bonds and 2 non-bonding electrons

Solution:



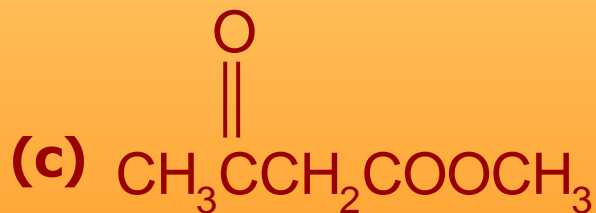
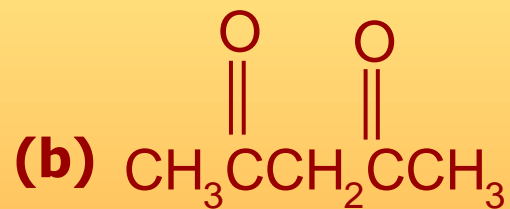
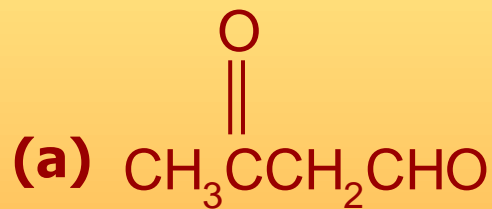
Allyl isocyanide

The compound has 3 π bonds and one lone pair, i.e. two non-bonding electrons. It also contains 9 σ -bonds.

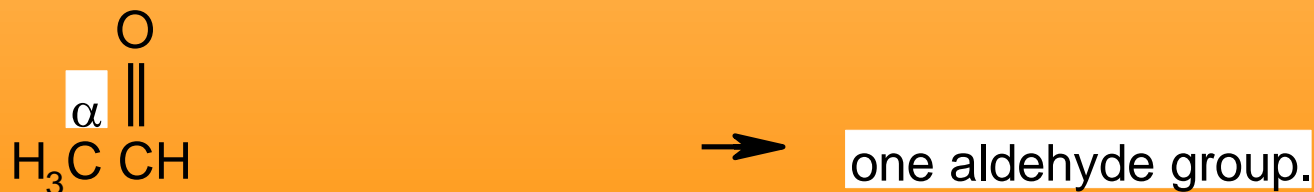
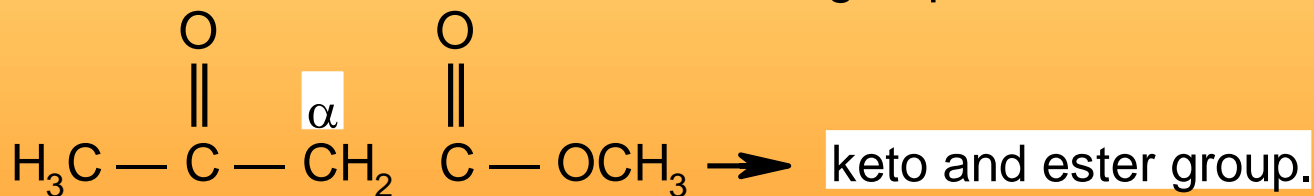
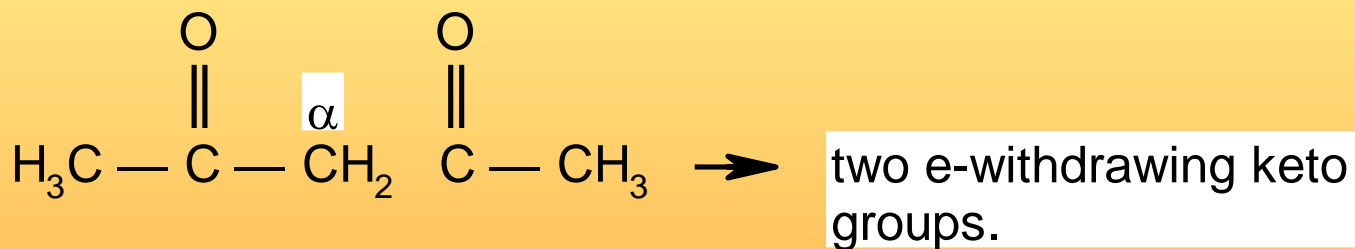
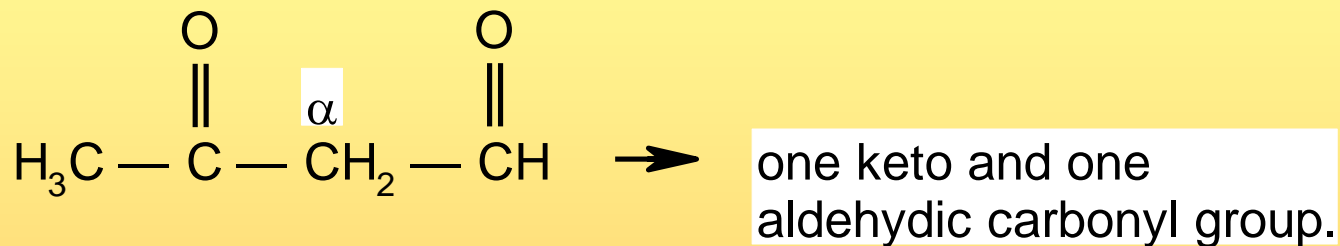
Hence answer is (d).

Class exercise 3

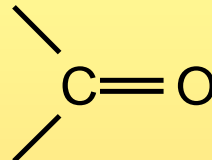
Among the following which has the most acidic α -hydrogen?



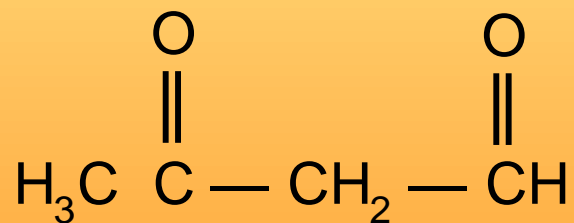
Solution



Solution

Since e-withdrawing nature of  gas varies as aldehyde > keto > ester

Then most acidic α -H atom is present in



Hence answer is (a).



Class exercise 4

The decreasing order of acidity among phenol, p-methylphenol, m-nitrophenol and p-nitrophenol is

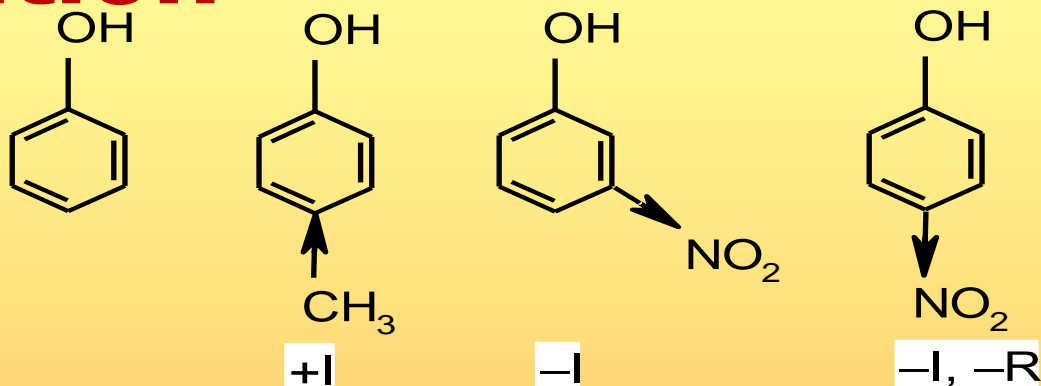
(a) m-nitrophenol, p-nitrophenol, phenol, p-methylphenol

(b) p-nitrophenol, m-nitrophenol, phenol, p-methylphenol

(c) p-methylphenol, phenol, m-nitrophenol, p-nitrophenol

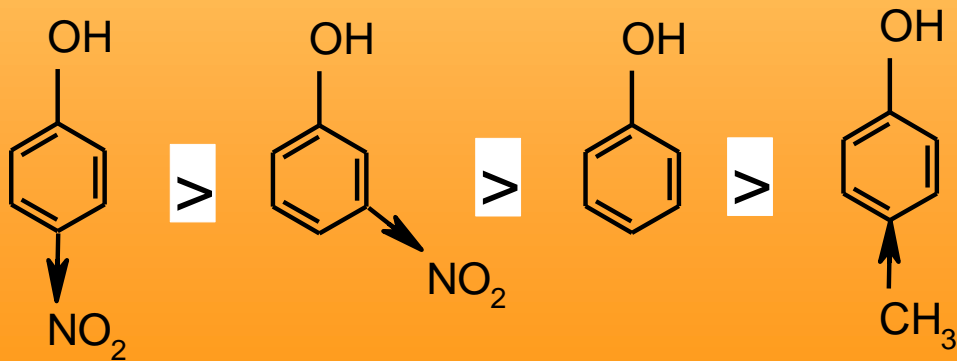
(d) phenol, p-methyl phenol, p-nitrophenol, m-nitrophenol

Solution



Electron withdrawing groups increase acidic strength while electron donating group decreases the same.

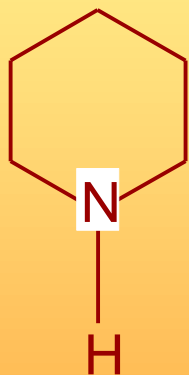
So the proper decreasing order of acidic strength is



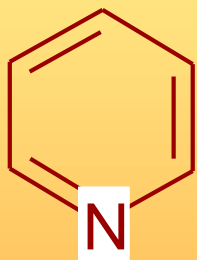
Hence answer is (b).

Class exercise 5

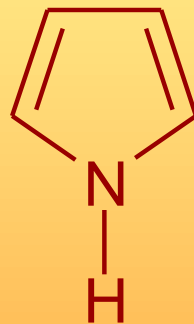
In the following compounds, the order of basicity is



(I)



(II) (III)



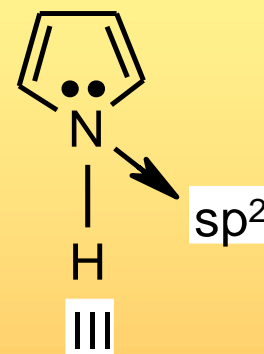
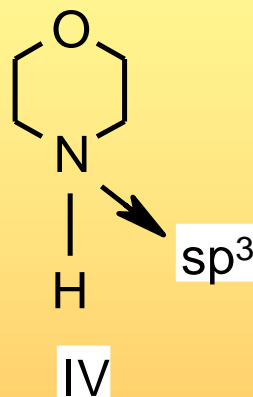
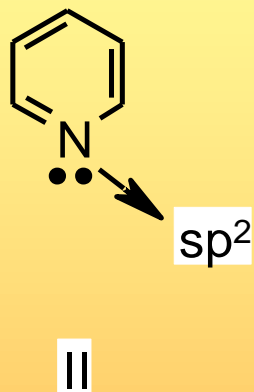
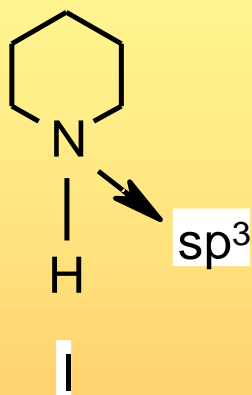
(IV)



(a) I > IV > II > I (b) II > I > IV > III

(c) III > I > IV > II (d) IV > I > III > II

Solution



Between I and IV, IV is less basic because of the $-I$ effect of oxygen atom.

II is more basic than III as the lone pair on N-atom in III is not available for protonation as it is involved in resonance.

Therefore, the correct order is $I > IV > II > III$

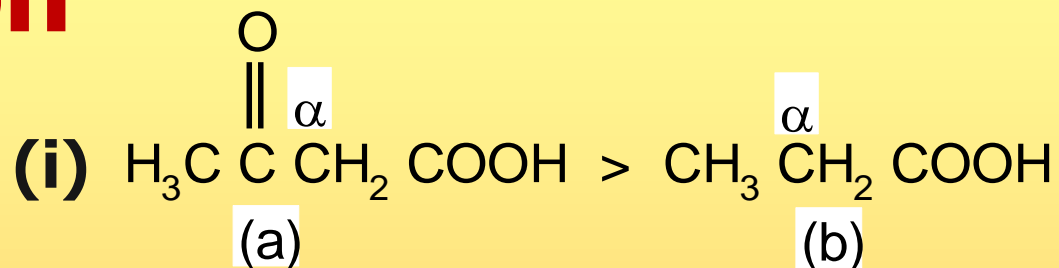
Hence answer is (a).

Class exercise 6

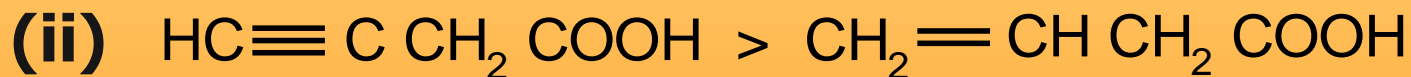
Account for the order acidity in the following compounds.



Solution



In compound (a), electron-withdrawing keto group increases the acidic strength by decreasing the O — H bond strength, while no such effect is there in compound (b).



Carbon atoms attached to triple bond is sp hybridised and more electron-withdrawing than sp^2 hybridised carbon atom.

Hence, such order in acidic strength is observed.



Class exercise 7

Which of the following two amines is more basic and why?

$\text{CCl}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ or $\text{CCl}_3\text{CH}_2\text{CH}_2\text{NH}_2$



Solution

Electron-withdrawing groups decrease the charge density on N-atom of organic amines and hence decrease the basic strength. In $\text{Cl}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, the electron withdrawing $-\text{CCl}_3$ is far apart from $-\text{NH}_2$ group as compared to $\text{Cl}_3\text{CCH}_2\text{CH}_2\text{NH}_2$.

Hence, the former is more basic in nature.

Class exercise 8



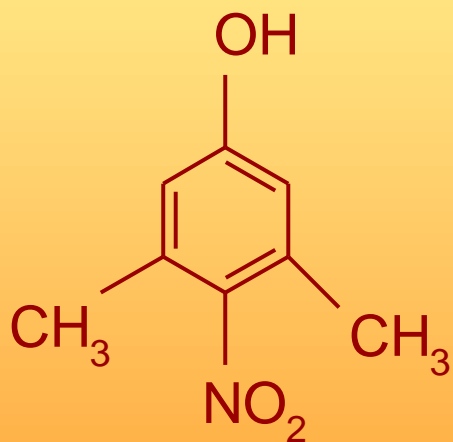
can show tautomerism?

Solution:

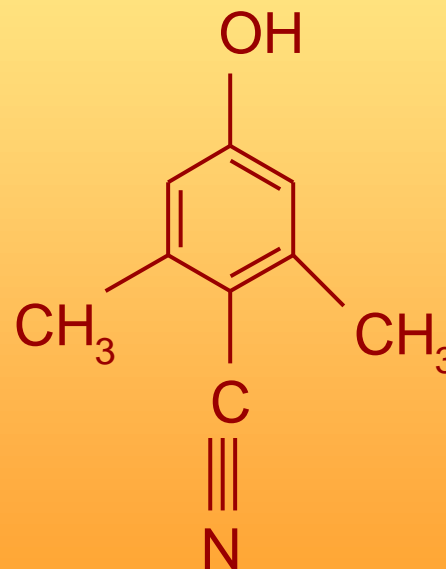
Yes. The tautomeric form is CH_3COCH_3 .

Class exercise 9

Which one will be more acidic ?



I



II

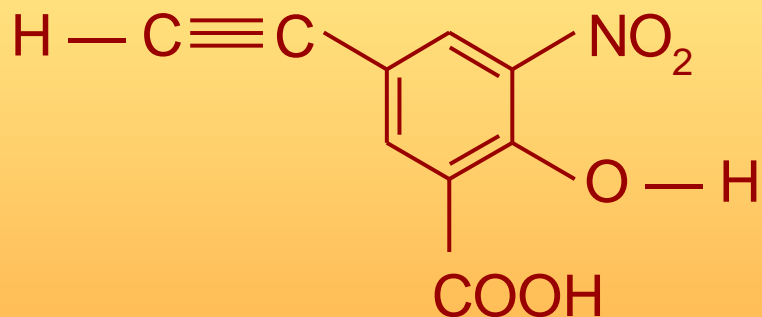


Solution

Because of steric inhibition of resonance conjugate base of I will not be stabilised by resonance. But for II there is no such steric inhibition of resonance.

Class exercise 10

Which hydrogen is maximum acidic in the following compound?



Solution:

Carboxylic hydrogen is maximum acidic.



Thanks...