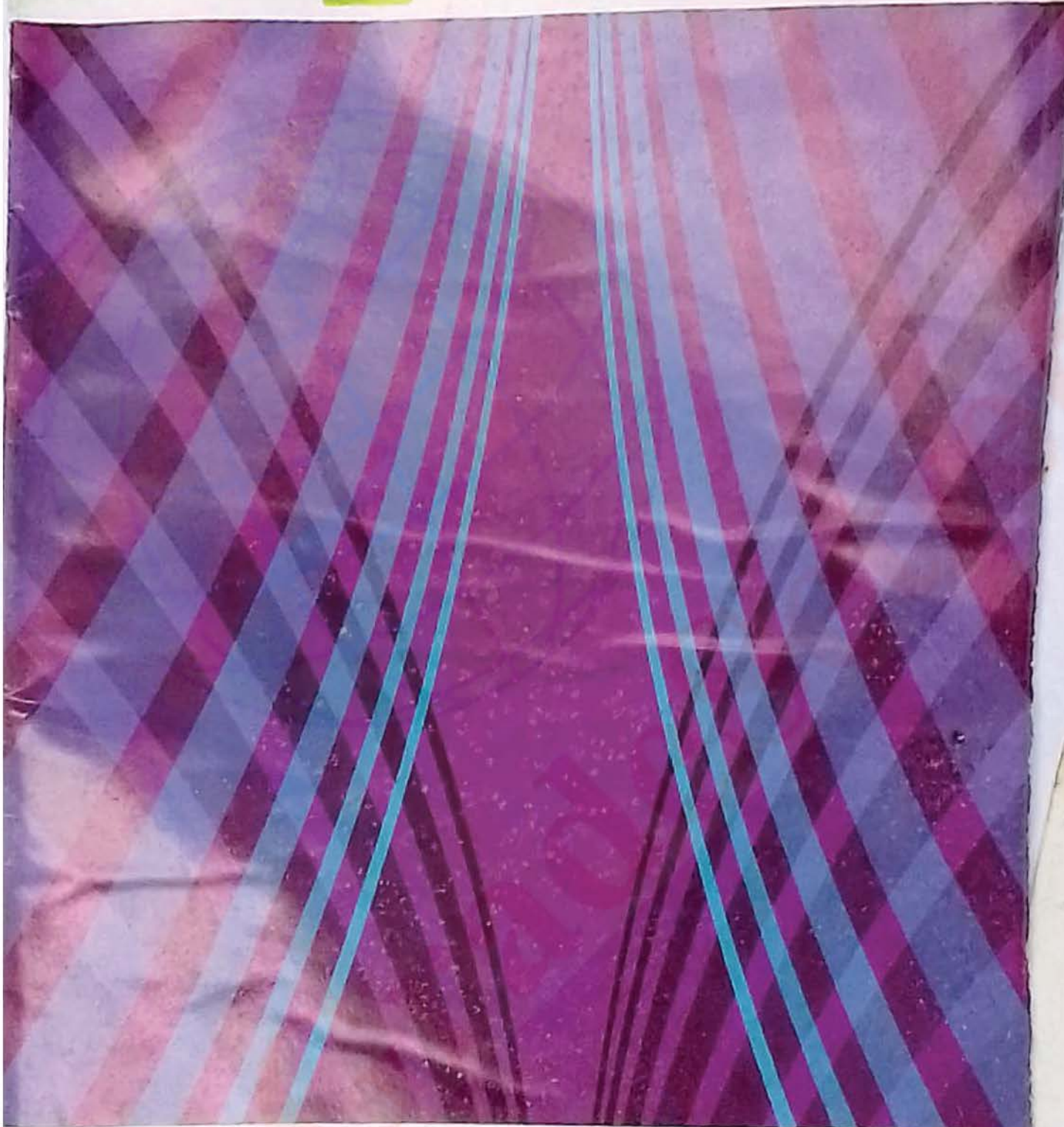




Resonance[®]
Educating for better tomorrow



CHEMISTRY

Target : JEE (Main)

GENERAL ORGANIC CHEMISTRY I

GENERAL ORGANIC CHEMISTRY-II

Contents

Topic	Page No.
Theory	01 – 15
Exercise - 1	16 – 25
Exercise - 2	25 – 31
Exercise - 3	31 – 35
Part - I : JEE (Main) /AIEEE Questions	
Part - II : JEE (Adv.)/ IIT-JEE Questions	
Answer Key	36
JEE-MAIN Practice Test Paper	37 – 41
JEE-MAIN Practice paper Answers	42
JEE-MAIN Practice Paper Solutions	42 – 43

JEE (Main) Syllabus

Bases, Acids & Tautomerism : Inductive, Resonance and Hyperconjugation Effect, Applications of Electronic Effects, Tautomerism and Acid-base.

JEE (Advanced) Syllabus

Fission of covalent bond: free radicals, electrophiles, nucleophiles, carbocations, carbonanions and tautomerism.

Acidic and basic strength of organic compounds.



General Organic Chemistry (GOC)-II

Applications of electronic effects :

1. Reaction Intermediates :

A covalent bond can get cleaved either by : (i) Homolytic cleavage or (ii) Heterolytic cleavage.

(i) **Homolytic bond dissociation** : A bond dissociation in which a bond pair electron is equally distributed to the bonding atoms.



a homolytic bond dissociation generates radicals.

(ii) **Heterolytic bond dissociation** : A bond dissociation in which a bond pair electron is shifted to one atom only.



A heterolytic bond dissociation always generate a cation and an anion.

(A) Carbanion :

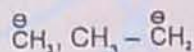
A carbon intermediate which contain three bond pair and a negative charge on it, is called carbanion.

Hybridisation : Carbanion carbon is in sp^3 hybridised state if it is linked to sp^3 hybridised carbon or hydrogen atoms, where as it will be in sp^2 hybridised state if it is linked to sp^2 hybridised C-atom due to resonance.

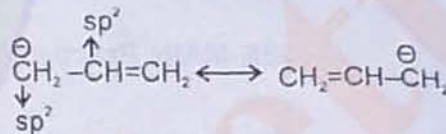
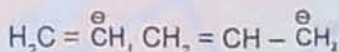
Hybridisation

Example

sp^3



sp^2



sp



Note : (i) Carbanion carbon is in sp^3 , sp^2 and sp hybridised state.

(ii) No rearrangement takes place.

(iii) It is diamagnetic ($8e^-$) in nature.

Stability of Carbanions : Followings factors increases the stability of carbanions.

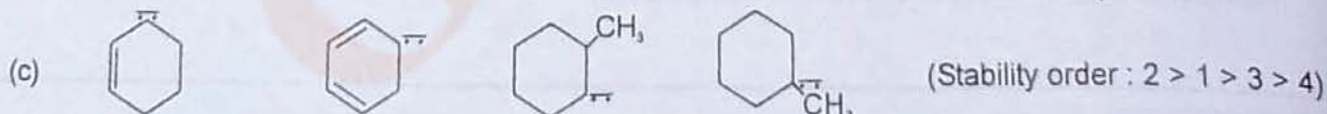
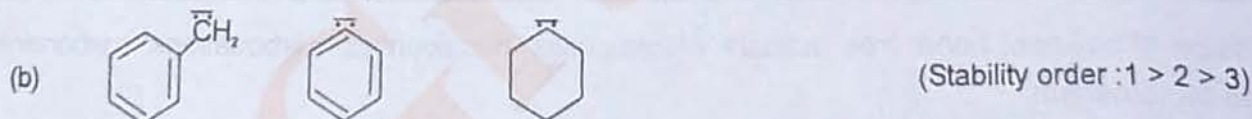
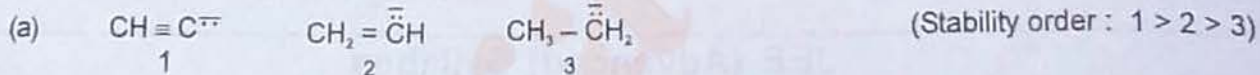
(i) -M effect

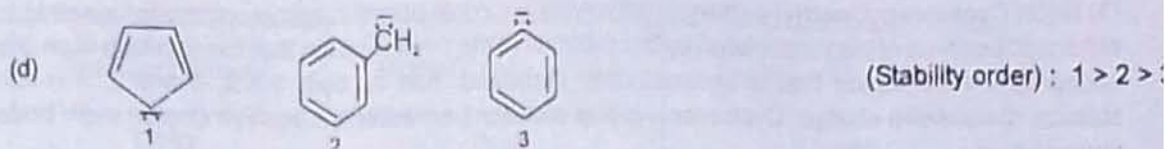
(ii) Delocalisation of -ve charge

(iii) -I effect

Note : If α -position of a carbanion has a functional group which contains multiple bond ($C=C$, $C=O$, $C\equiv N$, NO_2 etc) then carbanions are stabilised by resonance.

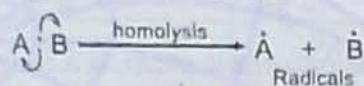
Example of stability order :



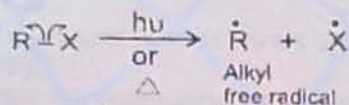


(B) Free Radicals :

Homolysis of covalent bond results into free radical intermediates possess the unpaired electrons.



It is generated in presence of Sunlight, Peroxide or high temperature



- (i) It is a neutral species with odd electron.
- (ii) It is paramagnetic in nature due to odd electron.
- (iii) No rearrangement is observed generally.
- (iv) Carbon atom having odd electron is in sp^2 hybridised state and 7 e^- in its valence shell.
- (v) Usually O_2 is used as inhibitor to slow down the radical reaction.
- (vi) Any reaction if it is carried out in the presence of sunlight, peroxide or high temperature proceeds via free radical intermediate.

Stability of free radical: It is stabilised by resonance, hyperconjugation and + I groups.

stability order $(C_6H_5)_3 C^\cdot > (C_6H_5)_2 CH^\cdot > C_6H_5 CH_2^\cdot > CH_2 = CH - CH_2^\cdot > 3^\circ > 2^\circ > 1^\circ > \dot{C}H_3$

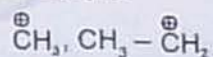
(C) Carbocation :

A carbon intermediate which contain three bond pair & a positive charge on it, is called carbocation. It is an electron deficient, diamagnetic species and rearrangement can be possible if stability is high.

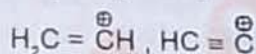
Hybridisation

Example

sp^2



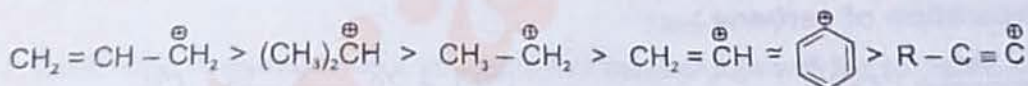
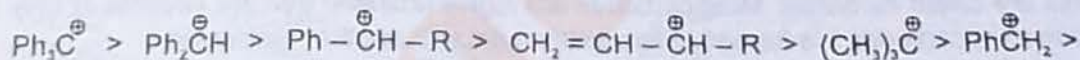
sp



Stability of carbocations : Following factors increases the stability of carbocations

- (i) + m effect
- (ii) Resonance stabilization
- (iii) Hyperconjugation
- (iv) + I effect

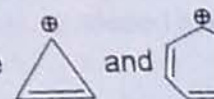
General stability order :



Note : (1) The carbocation is not possible at following bridge head positions I and II



(2) Carbocations showing aromatic behaviour are exceptionally more stable

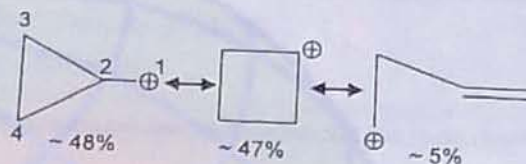


carbocations

General Organic Chemistry-II



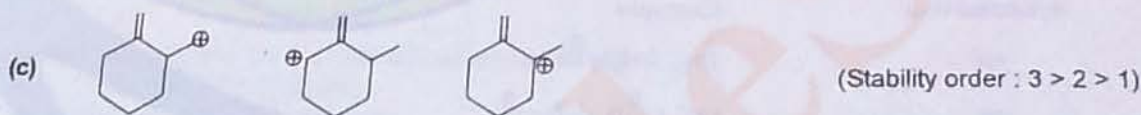
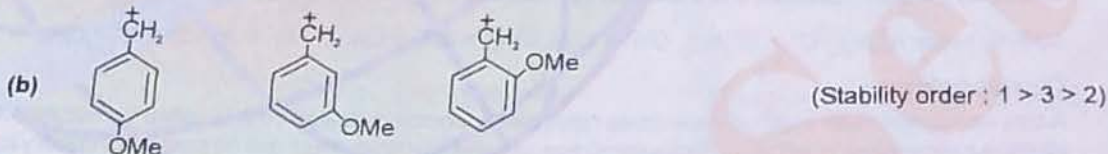
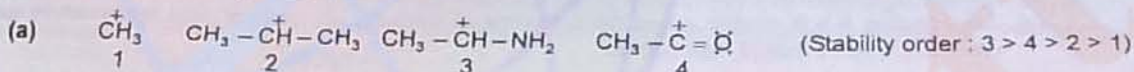
(3) **Note: Cyclopropylmethyl cation:** In solvolysis of simple primary cyclopropylmethyl systems the rate is enhanced because of the participation by the σ -bonds of the rings. The ion that forms initially is an unarranged cyclopropylmethyl cation that is symmetrically stabilized, that is, both the 2, 3 and 2, 4 σ -bonds help stabilize the positive charge. Cyclopropyl group stabilizes on adjacent positive charge even better than a phenyl group.



This special stability, which increases with each additional cyclopropyl group, is a result of conjugation between the bend orbitals of the cyclopropyl rings's and the vacant P-orbital of cationic carbon.



Examples of stability order :



(D) **Carbenes (Divalent Carbon intermediates) :**

Definition : There is a group of intermediates in which carbon forms only two bonds. These neutral divalent carbon species are called carbenes. Most carbenes are highly unstable that are capable of only fleeting existence. Soon after carbenes are formed, they usually react with another molecules.

Methods of preparation of carbene :



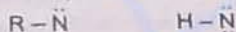
General Organic Chemistry-II

Types of carbene	Singlet $\overset{\cdot\cdot}{\text{C}}$	Triplet $-\overset{\cdot}{\text{C}}-\cdot$
Shape	Bent	Linear
Hybridisation	sp^2	sp
Nature of reaction	stereospecific	None
State	Excited state	Ground state
Magnetic	Diamagnetic	Paramagnetic
Nature	Paired electrons	Diradical

(E) Nitrenes

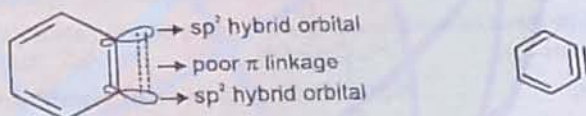
The nitrogen analog of carbenes are nitrenes. They are very much reactive since in them octet of N is incomplete.

In nitrenes only one valency of N is satisfied



(F) Benzyne

The benzene ring has one extra C-C π bond in benzyne



Clearly, we can see that the newly formed π bond cannot enter in resonance with other π orbitals of ring, since it is in perpendicular plane. It is also important to note that hybridisation of each carbon involved in 'Benzyne bond' is sp^2 since the overlap between these sp^2 hybrid orbitals is not so much effective.

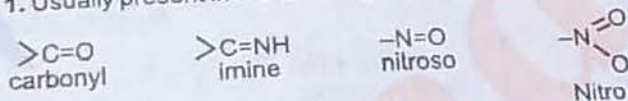
2. Tautomerism :

Definition :

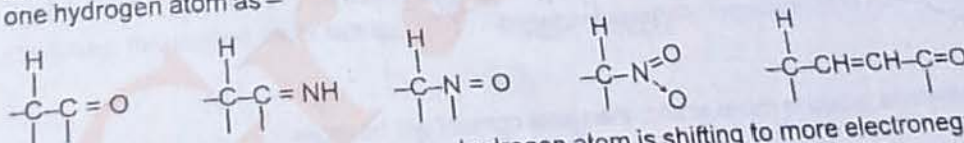
Tautomerism is a phenomenon by which a single compound exists in two or more readily interconvertible structures that differ in the relative positions of at least one atomic nucleus, generally hydrogen. These two isomers remain in dynamic equilibrium, can be isolated and also give different lab test.

Conditions :

1. Usually present in the following functional groups

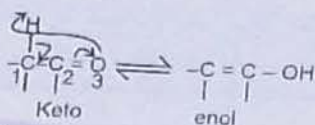


2. Basic need for its existence is attachment of these groups with the sp^3 hybridised C-atom having at least one hydrogen atom as -

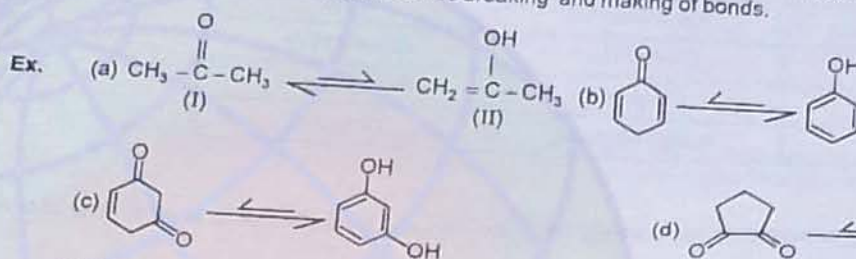


To get tautomer of above structures α -hydrogen atom is shifting to more electronegative atom attached to double bond (i.e. hydrogen atom from 1st atom to 3rd atom) and double bond is developed between 1,2-atom from 2,3-atom. This can be represented as :

General Organic Chemistry-II

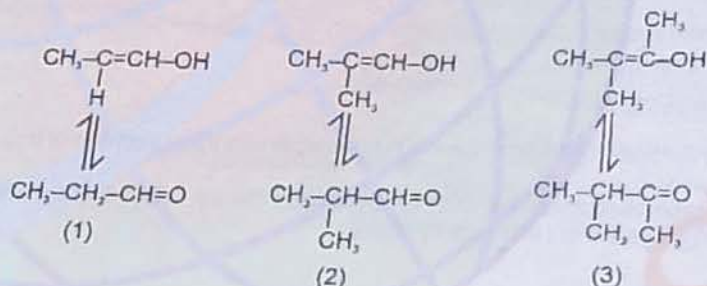


These two forms (remain in equilibrium) are called tautomers of each other. The interconvertibility of tautomers is a chemical reaction which involves breaking and making of bonds.



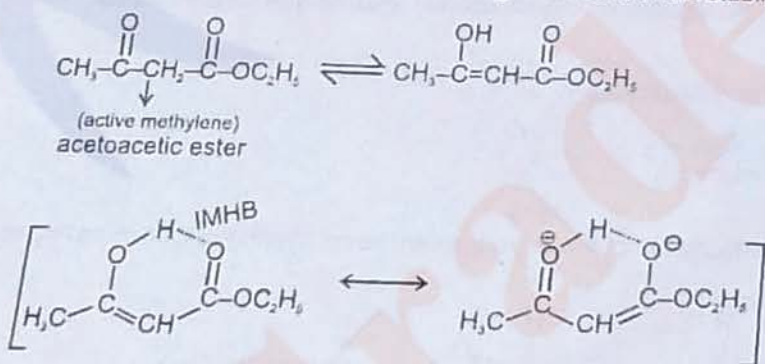
% Enol content in the carbonyl compounds :

- (i) For monocarbonyl generally it is very less.
- (ii) Enol content increases with increase in the stability of enol by hyperconjugation, hydrogen bonding, resonance etc.



Decreasing order of enol content for above carbonyl compounds is : 3 > 2 > 1.

(iii) For a carbonyl compound having active methylene group percentage of enol content will be more because enolic form has intramolecular H-bonding and also it will be stabilised by resonance.

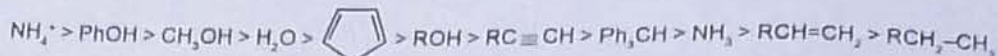
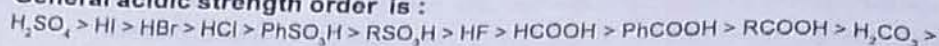


(iv) If active methylene group is more acidic, then enol content will be more.

For example in acetyl acetone ($\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$) enolic content is 75-76% while it is 7-8% in acetoacetic ester because ester group shows less electron withdrawing nature than keto group.

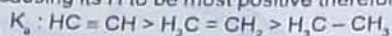
General Organic Chemistry-II

General acidic strength order is :



(B) Relative acidity of hydrocarbons :

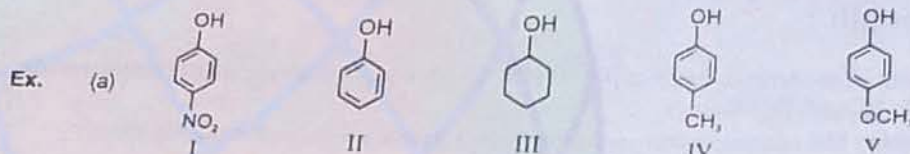
Being most electronegative the sp hybridised carbon atom of ethyne polarizes its $C-H$ bond to the greatest extent causing its H to be most positive therefore ethyne is most acidic hydrocarbon.



(C) Acidity of Phenols :

The phenoxide ion is more stabilised by resonance than the unionised phenol.

$-I, -m$ groups increases acidic character of phenol because effectively dispersing the negative charge of phenoxide ion. Alternatively $+I$ and $+m$ groups decreases acid strength.

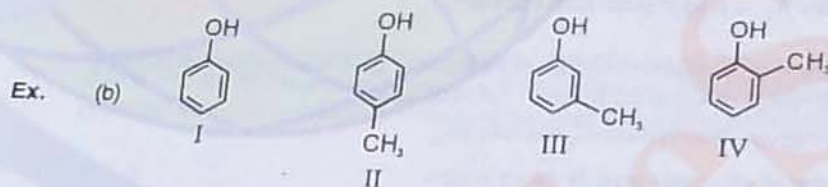


Ans. acid strength order : $I > II > IV > V > III$

Sol. **Step-1 :** III will be least acidic as it has no dispersion of negative charge (No delocalisation of negative charge).

Step-2 : Since $-I, -m$ group will increase acid strength, Nitrophenol will be most acidic followed by phenol.

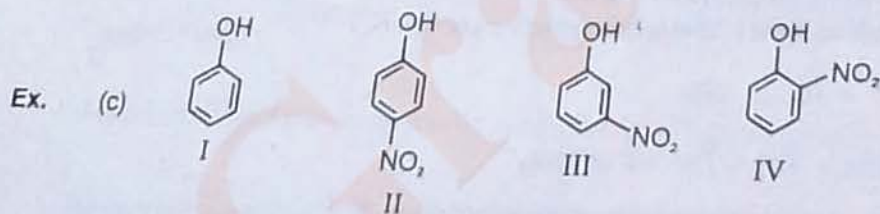
Step-3 : Amongst cresol and methoxyphenol, methoxyphenol has $+m$ effect of $-OCH_3$, which increases e^- density hence decrease acidic strength.



Ans. Acid strength order : $I > III > II > IV$

Sol. **Step-1 :** Notice that CH_3 has $+I$ effect so all methylphenols (cresols) are less acidic than phenol (I).

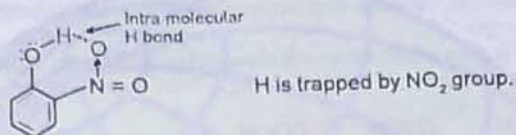
Step-2 : Now amongst cresols p - and o - CH_3 are increasing the e^- density due to their hyper conjugation but ortho isomer has viable $+I$ effect also, which will help in destabilising phenoxide ion therefore o - is least acidic. Since at meta position only $+I$ works, so it has least e^- density amongst the cresol.



Ans. Acid strength order : $II > IV > III > I$

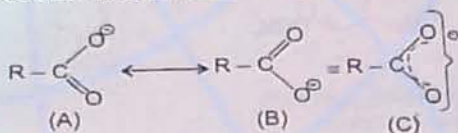
General Organic Chemistry-II

Sol. **Step-1** : In nitrophenols -I effect of NO_2 will help to increase acidic strength hence phenol is least acidic amongst all nitrophenols
Step-2 : Only -I effect is applicable in meta nitrophenol so it will be number three. Now -o, -p have both -I and -m effect of NO_2 group over OH and in this particular case para isomer is more acidic than ortho nitro phenol because of intramolecular H-bond.

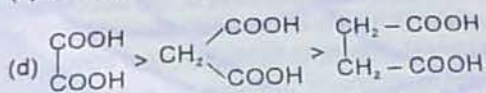
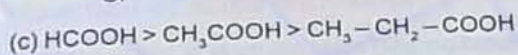
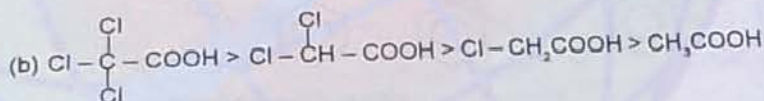
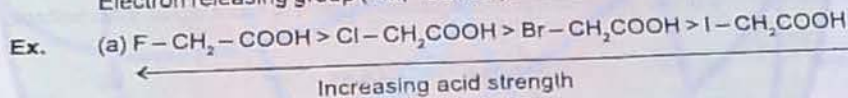


(D) Acidity of carboxylic acids :

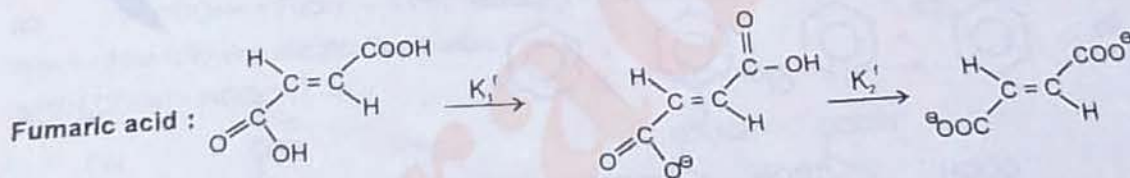
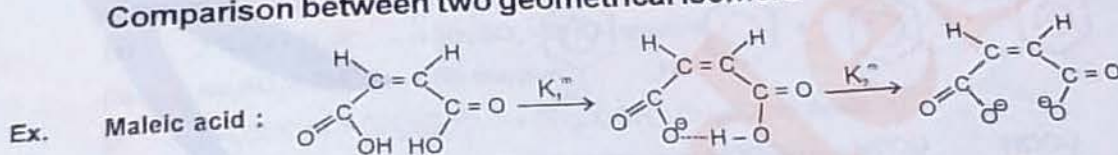
Conjugate base of carboxylic acid exists as two equivalent canonical structures (A) and (B). This ion is resonance stabilised and resonance hybrid structure is (C).



Electron withdrawing group (-M, -I effect) **increases** acidic nature.
 Electron releasing group (+M, +I effect) **decreases** acidic nature.



Comparison between two geometrical isomers



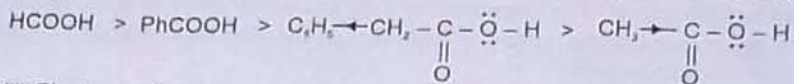
Now $K_1^m > K_1^f$
 Since the conjugate base is stabilised by intramolecular H bonding.

But $K_2^f > K_2^m$ Since in maleate ion, after donation of H^+ two $-\text{COO}^-$ groups faces each other and makes system unstable. In fumarate ion this repulsion is less.



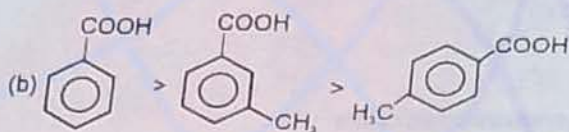
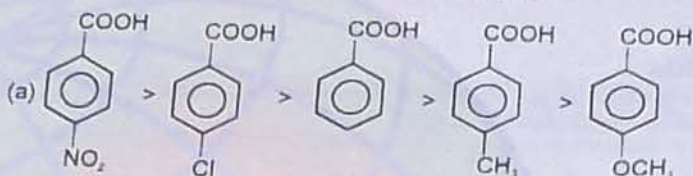
Acidic strength of substituted benzoic acid :

(i) Formic acid is more acidic than benzoic acid while phenyl acetic acid is more acidic than acetic acid.

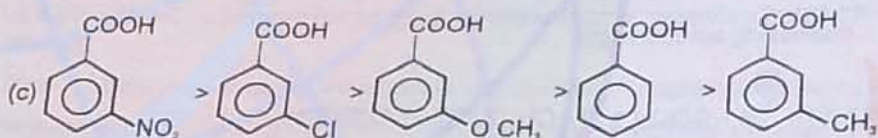


(ii) Electron withdrawing group attached to benzene ring will increase the acidic strength while electron releasing group decreases acidic strength.

(iii) If electron donating group present at para position then it is always less acidic than benzoic acid and also it is less acidic than meta substituted benzoic acid.

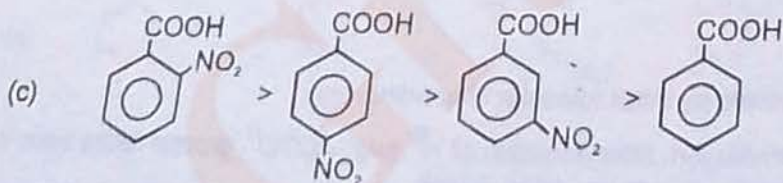
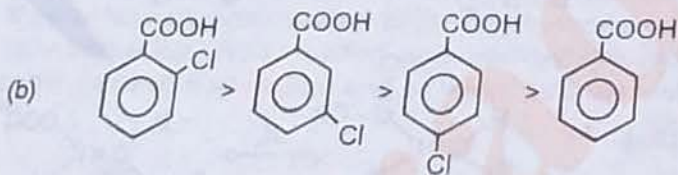
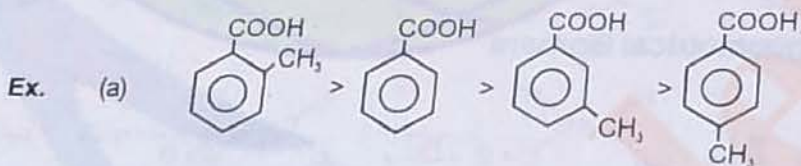


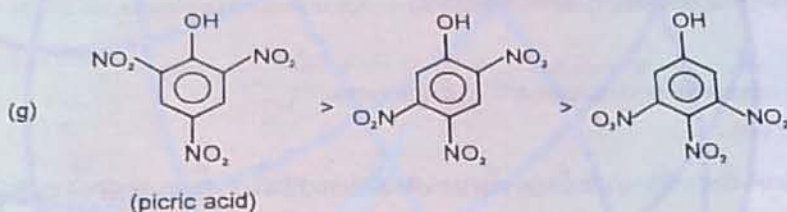
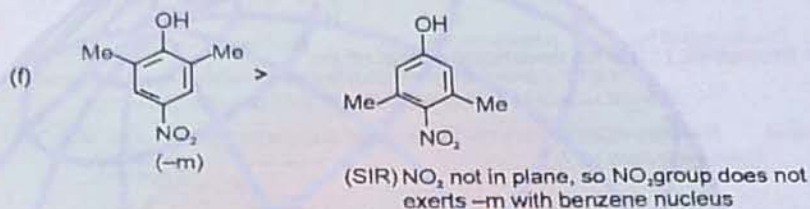
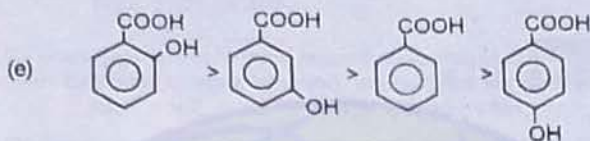
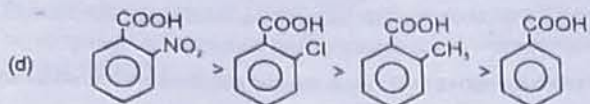
(v) On the other hand if e⁻ withdrawing group is present at meta position than it is more acidic than benzoic acid.



Ortho effect :

It is common observation that generally ortho substituted benzoic acids are more acidic as compared to their isomers and benzoic acids itself. This is called **ortho effect** (which is combined effect of steric hindrance, crowding & electronic effect) in ortho substituted benzoic acid. However exceptions are seen.





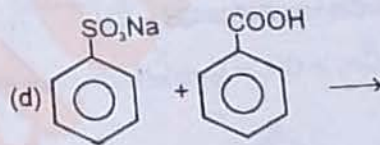
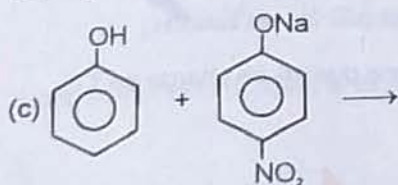
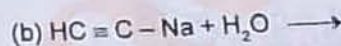
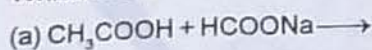
(E) Reaction of acids with salts :



Remark : A stronger acid displaces the weaker acid from weak acid metal salt. The weaker acid is released out as a gas or liquid or precipitate out as a solid. The weaker acid cannot displace the stronger acid from the salt.

- (a) $2 \text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$ (feasible)
- (b) $\text{Na}_2\text{SO}_4 + 2\text{HCl} \longrightarrow$ No reaction
- (c) $\text{CH}_3\text{COONa} + \text{CH}_3\text{SO}_3\text{H} \longrightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{SO}_3\text{Na}$ (feasible)
- (d) $\text{CH}_3\text{COONa} + \text{PhOH} \longrightarrow \text{PhONa} + \text{CH}_3\text{COOH}$ (not feasible)

Que. Which of the following reaction is possible ?

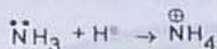


Ans. (a) Not possible (reverse is possible) (b) Possible (c) Not possible (d) Not possible

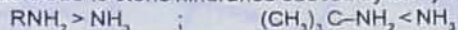
General Organic Chemistry-II

(C) Basic strength of aliphatic nitrogenous base :

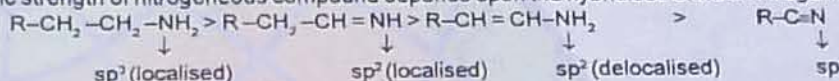
In nitrogenous compound basic strength is due to presence of lone pair of electrons at nitrogen atom which accept the proton.



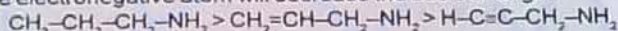
Note : (1) Usually 1° amine is more basic than ammonia but if alkyl part of 1° amine is tertiary butyl then NH₃ is more basic due to steric hindrance caused by bulky nature of tertiary butyl group.



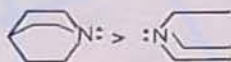
(2) Basic strength of nitrogenous compound depends upon the hybridised state of nitrogen.



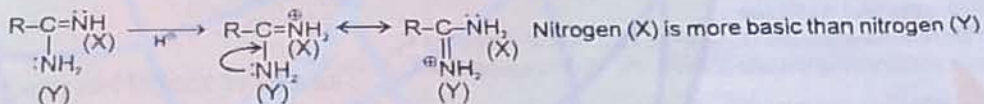
(3) More electronegative atom will decrease the basic strength.



(4) Cyclic amines are more basic than acyclic amines of same nature.



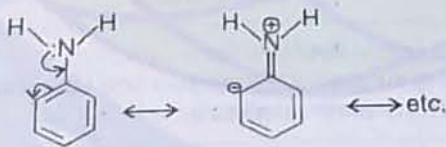
(5) Amidines are more basic in nature because their conjugate acid is more stable due to resonance.



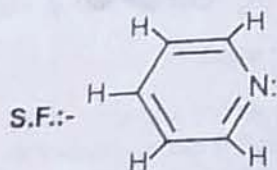
(D) Basic Strength of Aromatic Amines and substituted Anilines :

(a) Aniline :

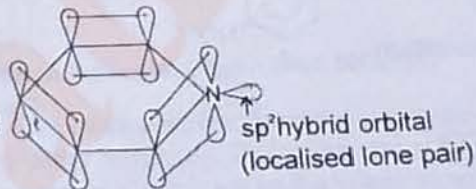
Lone pair of aniline lies in conjugation with a multiple bond, it resides in '2p' atomic orbital, so that it can get resonance stabilisation and hence, basic strength decreases. So, Aniline is a weaker base than NH₃



(b) Pyridine (C₅H₅N) : 6-π electrons, aromatic



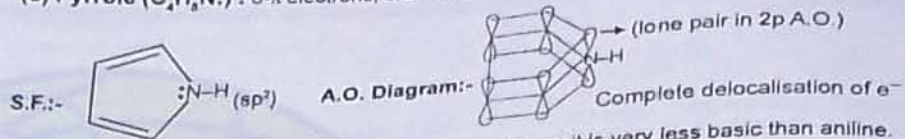
A.O. Diagram:



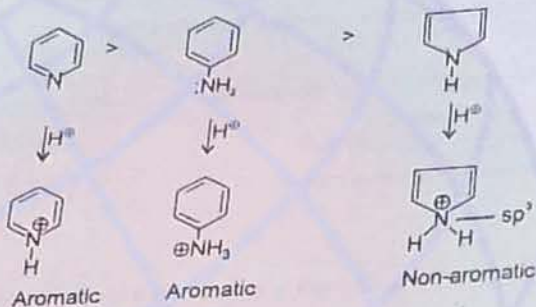
Lone pair of N in pyridine is localised so it is more basic than aniline.

General Organic Chemistry-II

(c) Pyrrole (C_4H_5N): 6- π electrons, aromatic



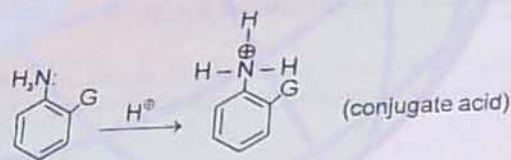
Lone pair of N in pyrrole is delocalised in the aromaticity so it is very less basic than aniline.



(d) Substituted Anilines :

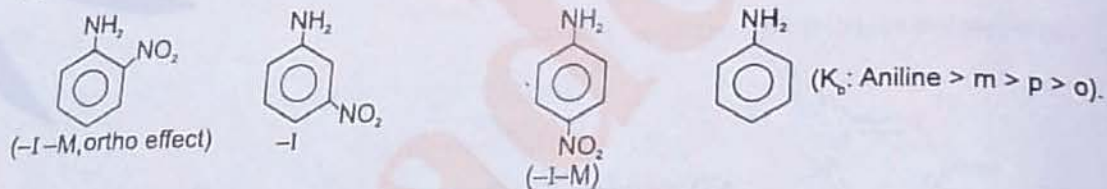
Electron releasing groups (ERG) +m, HC, +I increases the K_b
 Electron withdrawing groups (EWG) -m, -I decreases the K_b

Steric effect of ortho-substituent in Aniline (ortho effect) :

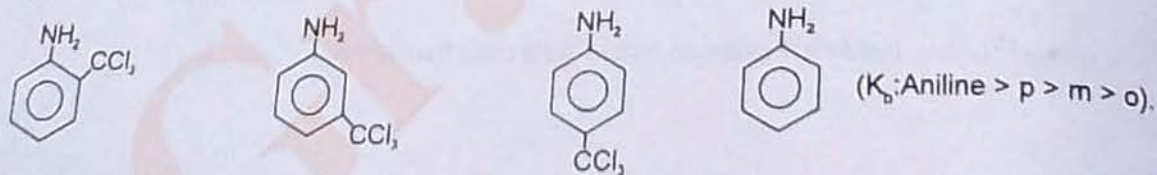


- (i) Ortho-substituted anilines are mostly weaker bases than aniline itself.
- (ii) Ortho-substituent causes steric hinderance to solvation in the product (conjugate acid i.e. cation).
- (iii) The small groups like -NH₂ or -OH do not experience (SIR) due to small size.

Ex. (a) G = (-M, -I); NO₂



(b) G = (-I); CCl₃



Only (-I) decides the order.

RESONANCE STUDY CENTRES (Self Owned)

KOTA (Head Office):

Pre-Engineering Division, JEE (Advanced)
Pre-Engineering Division, JEE (Main)
Pre-Medical Division, AIIMS/ AFMT
Tel: 0744-3012222, 3192222, 6635555
e-mail: contact@resonance.ac.in

Commerce & Law Program Division (CLPD)

Tel: 0744-3192221, 6060663
e-mail: clpd@resonance.ac.in

PCCP/PSPD/MEs

Tel: 0744-2434727, 8824076330, 3192223, 2440488
e-mail: pcpp@resonance.ac.in

DLPO

Tel: 0744-6635556, 3012222
e-mail: dlpo@resonance.ac.in

eLPO

Tel: 0744-3058242
e-mail: elpo@resonance.ac.in

JAIPUR

Tel: 0141-6060661/64, 3103666, 6060662/63
e-mail: jaipur@resonance.ac.in

BHOPAL

Tel: 0755-3206353, 3192222, 3256353
e-mail: bhopal@resonance.ac.in

NEW DELHI

Tel: 011-6060660/1/2/3/4/5/6/7
e-mail: delhi@resonance.ac.in

LUCKNOW

Tel: 0522-3192222, 3192223/4, 6060660/61/62
e-mail: lko@resonance.ac.in

KOLKATA

Tel: 033-3192222, 6060660/01/02
e-mail: kolkata@resonance.ac.in

NAGPUR

Tel: 0712-3017222, 3192222, 6060660
e-mail: nagpur@resonance.ac.in

HANDELI

Tel: 02462-250220, 6060660
e-mail: handeli@resonance.ac.in

MUMBAI

Tel: 022-3192222, 6060660
e-mail: mumbai@resonance.ac.in

UDAIPUR

Tel: 0294-6060660, 5107510, 3192222
e-mail: udaipur@resonance.ac.in

BHUBANESWAR

Tel: 0674-3192222, 3274918, 6060660/61
e-mail: bbsr@resonance.ac.in

AHMEDABAD

Tel: 079-3192222/3/4 & 079-6060660/1/2
e-mail: ahmed@resonance.ac.in

PATNA

Tel: 0612-3192222, 3192222/3
e-mail: patna@resonance.ac.in

JODHPUR

Tel: 0291-6060660
e-mail: jodhpur@resonance.ac.in

AJMER

Tel: 0145-3192222, 6060660/65
e-mail: ajmer@resonance.ac.in

INDORE

Tel: 0731-3192222, 4274200
e-mail: indore@resonance.ac.in

SIKAR

Tel: 01572-3192222, 6060660
e-mail: sikar@resonance.ac.in

AGRA

Tel: 0562-3192222, 6060660
e-mail: agrs@resonance.ac.in

RANCHI

Tel: 0651-6060660
e-mail: ranchi@resonance.ac.in

ALLAHABAD

Tel: 0532-6060660
e-mail: allahabad@resonance.ac.in

NASHIK

Tel: 0253-6090026
e-mail: nashik@resonance.ac.in

RAIPUR

Tel: 0771-6060660
e-mail: raipur@resonance.ac.in

AURANGABAD

Tel: 0240-6060660
e-mail: aurgabad@resonance.ac.in

JABALPUR

Tel: 0761-6060660
e-mail: jabalpur@resonance.ac.in

GWALIOR

Tel: 0751-6060660
e-mail: gwalior@resonance.ac.in

CHANDRAPUR

Tel: 07172-6060660
e-mail: chandrapur@resonance.ac.in

SURAT

Tel: 0261-6060660
e-mail: surat@resonance.ac.in

RAJKOT

Tel: 0281-6002011
e-mail: rajkot@resonance.ac.in

VAODARA

Tel: 0265-6060660
e-mail: vadodara@resonance.ac.in

BASE STUDY CENTRES

Base Education Service Pvt. Ltd.

Bengaluru (Main Branch):

Reg. Office: No.27, Next to Indian Oil

Petrol Bunk, Bull Temple Road,

Basavanagudi, Bengaluru-560004

Tel. No.: 42604600/9538141504

E-Mail: info@base-edu.in

Website: www.base-edu.in

BANASANKARI II STAGE

Tel: 26710835/26710836

BELAGAVI

Tel: 0831-4208687 | Mobile: 9845226000

CHITRADURGA

Mobile: 9886464755, 9972413844

HUBLI

Tel: 0836-2252685 | Mobile: 9844118615

INDIRANAGAR

Tel: 41179342/25201306

KALYAN NAGAR

Tel: 080-25443363/25443364

KORAMANGALA

Tel: 40925512/40925534

MALLESHWARAM

Tel: 41400008

MYSURU

Tel: 0821-4242100/4258100/4243100

RAJAJINAGAR

Tel: 08023327588/41162135

SHIVAMOGGA

Tel: 08182-223980, 8884849590

TUMAKURU

Tel: 0816-2252387

UDUPI

Tel: 0820-2522449, 2522994, 9986663074

VIJAYANAGAR

Tel: 23111333/23111334

YELAHANKA

Tel: 08028463922/42289643

CHIKKAMAGALURU

Mobile: 7411329369, 9448396690

HASSAN

Mobile: 9481392014, 9972038293

J P NAGAR

Tel: 26595151/26595153

KALABURGI

Tel: 08472-230914
Mobile: 9845905200/9844510914



Resonance[®]
Educating for better tomorrow

Corporate Office: CG Tower, A-46 & 52, IPHA, Near City Mall, Jhalawar Road, Kota (Rajasthan)- 324005
Reg. Office: J-2, Jawahar Nagar Main Road, Kota (Raj.)- 05 | Tel. No.: 0744-3192222, 3012222, 6635555 | CIN: U80302RJ2007PLC024029
To Know more: sms RESO at 56577 | E-mail: contact@resonance.ac.in | Website: www.resonance.ac.in