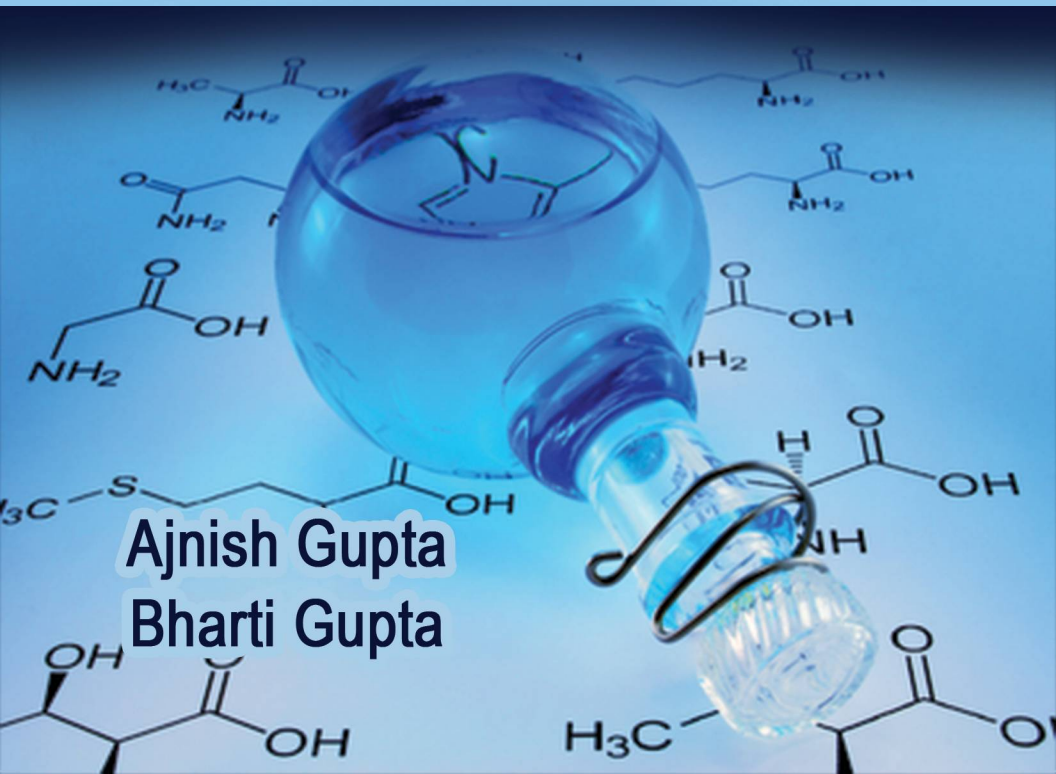
Problem Solving Strategy of NCERT -

Organic Chemistry Questions



Ajnish Gupta
Bharti Gupta

Problem Solving Strategy of NCERT

Organic Chemistry

Questions

By

AJNISH GUPTA & BHARTI GUPTA
Professor of Organic Chemistry

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Preface

The guiding principle in writing this book was to create a textbook for students- **a textbook that presents the material in a way that they learn** to solve all the questions of NCERT along with the strategy to approach the problems.

In this book we mixed all our teaching experience of 10 years along with theoratical and experimental knowledge to generate a hand book for all students to reason their way to a solution rather than memorize a multitude of facts, hoping they don't run out of memory.

If you ask your teacher, senior or friend about NCERT, then they will surely say that NCERT questions are very important to solve before giving board exam or any competitive exam as it is the basic theme for any board or competitive exam and nearly all the questions are derieved from NCERT only.

But the problem in NCERT organic chemistry is that there are a lot of intermixing of concept involve in same chapter so many students get fear of it and generally leave it by thinking that they can score good marks or rank without it, but they are fooling themself.

Organic chemistry is very easy and conceptual subject and need proper understanding of the basics and stretegy to solve the questions in corret manner.

This book will prepare your right mindset for learning Organic Chemistry. This mindset is essentially the one that focuses you on a small number of straight forward, repeated, fundamental concepts and helps you to apply them in different ways to solve the variety of problems you face in NCERT or other organic problems.

Ajnish Kumar Gupta & Bharti Gupta

Acknowledgement

We are thankful to all the teachers who taught us during the concept building session of our life specially Dr. Nizamuddin sir, senior Chandra Vijay Rao and Dr. Vijay Pratima Mittal madam.

We have written this book to remove the fever of organic chemistry from mind of students.

We particularly want to thank many wonderful and talented students whom we have taught over the years who in turn taught us how to be a good teacher and how we can help others.

We want to make this book as user friendly as possible, and we will appreciate any comments that will help us to achieve this goal in future editions.

Finally, this edition has been presented before you with efforts to make it errors free. Any that remain are our responsibility; if you find any, please let us know so they can be corrected in future printing.

Ajnish Gupta & Bharti Gupta
Professors of Organic Chemistry
Ajnish@OrganicChemistry.co.in
09122057123

Table of Contents

Dedication

Dedicated to all those students who are in fever of organic chemistry.

Unit 1

Organic Chemistry-
Some basic principles and Techniques

Objective

This unit give you an understanding of "Organic chemistry- Some basic principles and Techniques" and covers following topics:

- ☑ What is Organic chemistry, **Representation** of Organic compounds, Reason for the formation of large number of organic compounds, **Functional groups**, Homologue & Homologous series, Nature of C & H, functional groups, Saturated & unsaturated molecules, Hybridization, Classification of organic compounds, Alkyl groups, IUPAC nomenclature & Common name of Organic molecules.
- ☑ Basic understanding of isomerism in organic chemistry. **Structural isomerism**– Chain, Position, Function, Metamer, Tautomer. **Stereoisomerism**– Configurational & Conformational. Configurational– Geometrical & Optical isomerism.
- ☑ **Electronic effects-** Inductive effect, Basic concept of resonance, General cases of resonance, Electron flows in bond, How to draw resonating structures, Stabiity of resonating structrue, Mesomeric effect, Hyperconjugation, Electromeric effect;
  Reaction intermediate-Carbocation, Carbanion, Free radicals, Carbene, Nitrene, Benzyne;
  Concept of Acid and Base- How to find out relative Acidic & Basic strength, Scale to measure Acidic & Basic strength
- ☑ **Practical organic chemistry**- Methods of purification of organic compounds, qualitative & quantitative analysis of organic compounds.

Solved Example:

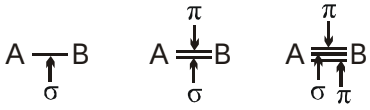
Example 1.

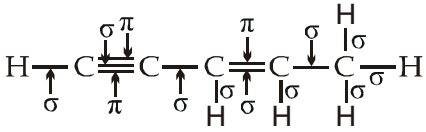
How many σ and π bonds are present in each of the following molecules?

(A) $HC \equiv CCH = CHCH_3$ (B) $CH_2 = C = CHCH_3$

Strategy.

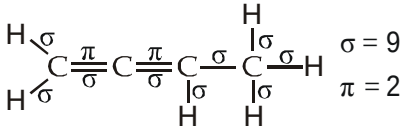
To solve such questions, always expand the structure and count the number of σ & π bond keeping given basic in mind.



(A) 

$\sigma = 10$

$\pi = 3$

(B) 

$\sigma = 9$

$\pi = 2$

Example 2.

What is the type of hybridisation of each carbon in the following compounds?

(A) CH_3Cl (B) $(CH_3)_2CO$

(C) CH_3CN (D) $HCONH_2$

(E) $CH_3CH = CHCN$

Strategy.

To find the hybridization of any atom, always count the number of σ bonds & lone pairs of electrons. If

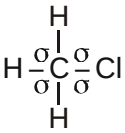
Sum of σ bond + lone pair of $e^- = 2 \Rightarrow sp$ hybridization

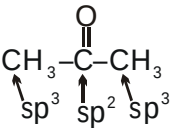
Sum of σ bond + lone pair of $e^- = 3 \Rightarrow sp^2$ hybridization

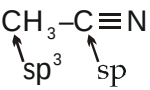
Sum of σ bond + lone pair of $e^- = 4 \Rightarrow sp^3$ hybridization

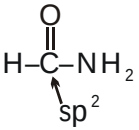
As carbon have no lone pair of electrons so always count the number of σ bonds in deciding the hybridization of carbon atom.

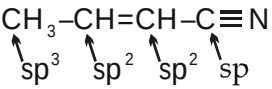
✓ There is no role of π bond in deciding the hybridization of any atom.

(A)  $4\sigma \Rightarrow sp^3$

(B) 

(C) 

(D) 

(E) 

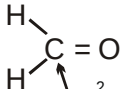
Example 3.

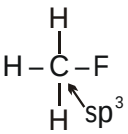
Write the state of hybridisation of carbon in the following compounds and shapes of each of the molecules.

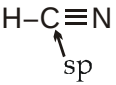
(A) $H_2C=O$ (B) CH_3F (C) $HC \equiv N$

Strategy.

Similar to above question, first expand the molecule & then count the number of σ bond for deciding the hybridization of carbon.

(A) 

(B) 

(C) 

As shape is the real structure of molecule which can be explained with the help of hybridization.

Generally following hybridization give following shape.

$sp \longrightarrow$ Linear

$sp^2 \longrightarrow$ Planner

$sp^3 \longrightarrow$ tetrahedral

So shape of A is planner, B is tetrahedral & C is linear.

Example 4.

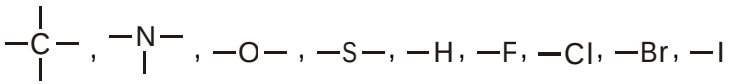
Expand each of the following condensed formulas into their complete structural formulas.

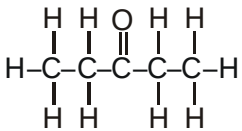
(A) $CH_3CH_2COCH_2CH_3$ (B) $CH_3CH=CH(CH_2)_3CH_3$

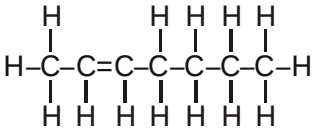
Strategy.

To expand the molecule in correct form, always keep in mind the valencies of some common atoms such as i.e. carbon always form 4 bonds in neutral case.

✓ Always keep this concept for making a neutral structure.



(A) 

(B) 

Example 5.

For each of the following compounds, write a condensed formula and also their bond-line formula.

(A) $HOCH_2CH_2CH_2CH(CH_3)CH(CH_3)CH_3$

(B) 

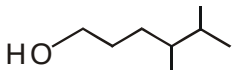
Strategy.

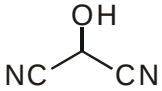
To write the condensed formula, always give $(CH_2)_n$ time for more than one CH_2 unit and $(CH_3)_n$ for CH_3 unit.

For bond line formula, write the molecule in zig-zag form.

(A) $HO(CH_2)_3CH(CH_3)CH(CH_3)_2$ (B) $CH(OH)(CN)_2$

zig-zag form.

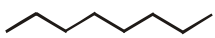


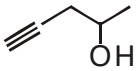


Example 6.

Expand each of the following bond-line formulas to show all the atoms including carbon and hydrogen.

(A) 

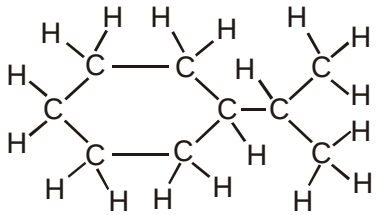
(B) 

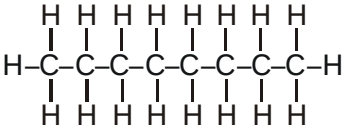
(C) 

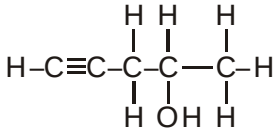
(D) 

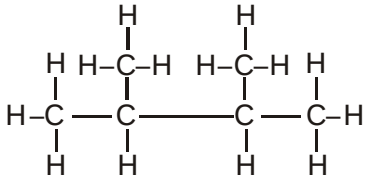
Strategy.

In bond line formula, the number of H at each carbon = 4 – no. of visible bond.

(A) 

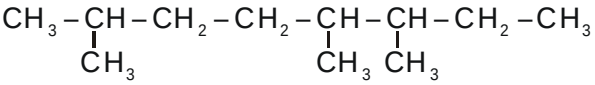
(B) 

(C) 

(D) 

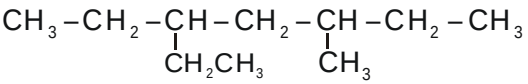
Example 7.

Structures and IUPAC names of some hydrocarbons are given below. Explain why the names given in the parentheses are incorrect.

(A) 

2,5,6-Trimethyloctane

[and not 3,4,7-Trimethyloctane]

(B) 

3-Ethyl-5-methylheptane

[and not 5-Ethyl-3-methylheptane]

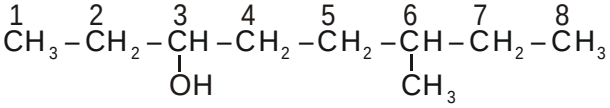
Strategy.

(A) In writing the IUPAC name of organic compound, always give minimum positions to substituents i.e. use lowest locant for substituent.

(B) In writing the IUPAC name of organic compound on identical position, numbering in chain starts according to alphabets of substituent. The alphabet which comes first are given lower position.

Example 8.

Write the IUPAC names of the compounds i-iv from their given structures.

(i) 

Strategy.

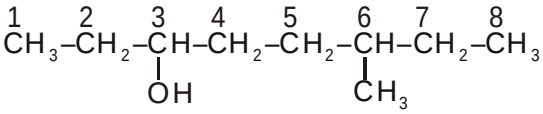
To write IUPAC name of any compound always use following keys

(A) Use the concept of 2°prefix + 1°prefix + Word root + 1°suffix + 2°suffix in sequence.

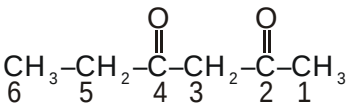
(B) Use the concept of position then alphabet then position if functional group, multiple bond or substituents are present.

(C) For giving minimum position $\Rightarrow$ functional group then multiple bond then substituent.

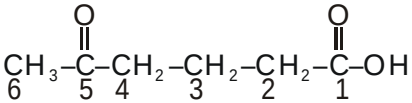
(D) If more than one functional groups are present, then use the concept of priority order.

(i) 

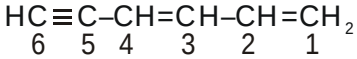
6-Methyloctan-3-ol

(ii) 

Hexane-2,4- dione

(iii) 

5-Oxohexanoic acid

(iv) 

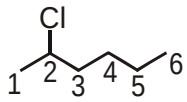
Hexa-1,3-dien-5-yne

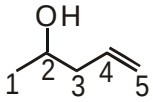
Example 9.

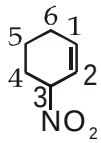
Derive the structure of (i) 2-chlorohexane, (ii) Pent-4-en-2-ol, (iii) 3-Nitrocyclohexene, (iv) Cyclohex-2-en-1-ol, (v) 6-Hydroxy-heptanal.

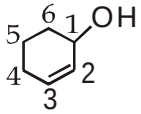
Strategy.

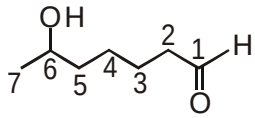
To make the structure from given name, always take the help of word root. Make the chain according to word root. Number them as 1, 2, 3 .... then place the substituent, multiple bond or functional group over it.

(i) 

(ii) 

(iii) 

(iv) 

(v) 

Example 10.

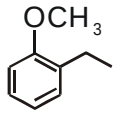
Write the structural formula of :

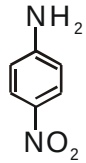
(A) o-Ethylanisole (B) p-Nitroaniline

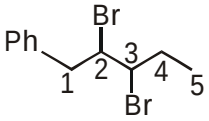
(C) 2,3-Dibromo-1-phenylpentane (D) 4-Ethyl-1-fluoro-2-nitrobenzene

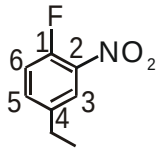
Strategy.

For disubstituted benzene, 2nd position is considered as ortho, 3rd position as meta & 4th position as para with respect to first substituent.

(A) 

(B) 

(C) 

(D) 

Example 11.

Using curved-arrow notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage.

(A) CH_3-SCH_3 (B) CH_3-CN

(C) CH_3-Cu

Strategy.

In heterolytic bond cleavage, bond breaks to acquire negative charge over more electronegative atom & positive charge over less electronegative atom.

(A) $CH_3-\overset{\curvearrowright}{S}-CH_3 \longrightarrow CH_3^{\oplus} + \overset{\ominus}{S}-CH_3$

(B) $CH_3-\overset{\curvearrowright}{C}N \longrightarrow CH_3^{\oplus} + \overset{\ominus}{C}N$

(C) $CH_3\overset{\curvearrowleft}{-}Cu \longrightarrow CH_3^{\ominus} + \overset{\oplus}{C}u$

Example 12.

Giving justification, categorise the following molecules / ions as nucleophile or electrophile:

$HS^-, BF_3, C_2H_5O^-, (CH_3)_3N:, \overset{+}{C}l, CH_3-\overset{+}{C}=O, H_2\bar{N}:, \overset{+}{N}O_2$

Strategy.

To solve this question, remember the basic definition of nucleophile & electrophile.

Nucleophiles- They are e^- rich species with complete octet with either negative charge or with lone pair of electrons.

Electrophiles- They are the e^- deficient species with either incomplete octet, vacant orbital or +ve charge over it.

So nucleophiles are $HS^-, C_2H_5O^-, (CH_3)_3N, H_2N^{\ominus}$ while electrophiles are $BF_3, Cl^+, CH_3-\overset{\oplus}{C}=O, \overset{\oplus}{N}O_2$

Example 13.

Identify electrophilic centre in the following:

$CH_3CH=O, CH_3CN, CH_3I.$

Strategy.

Electrophilic centre is the electron deficient centre in the molecule. They arises due to difference in electronegativity between two atoms so electrophilic centre in above molecules are

$CH_3\overset{\nwarrow}{H}C=O$ $H_3C\overset{\nwarrow}{C}\equiv N$ $H_3\overset{\nwarrow}{C}-I$

Example 14.

Which bond is more polar in the following pairs of molecules:

(A) H_3C-H, H_3C-Br (B) H_3C-NH_2, H_3C-OH

(C) H_3C-OH, H_3C-SH

Strategy.

Polarity of bond is judged on the basis of electronegativity difference. Greater is the electronegativity difference, greater is the polarity. So

(A) C–Br bond is more polar than C–H

(B) C–O bond is more polar than C–N

(C) C–O bond is more polar than C–S

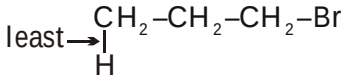
Example 15.

In which C–C bond of $CH_3CH_2CH_2Br$, the inductive effect is expected to be the least?

Strategy.

As inductive effect is distance dependent so magnitude of inductive effect diminishes as the number of intervening bond increases.

Hence, between 3rd carbon & hydrogen bond exert least inductive effect.

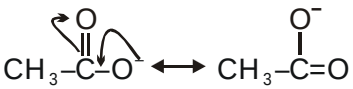


Example 16.

Write resonance structures of CH_3COO^- and show the movement of electrons by curved arrows.

Strategy.

To write resonating structure of any molecule, first write the structure of it and then put unshared electron or –ve charge on appropriate atoms, then draw arrow one at a time moving the electron to get the other structure.

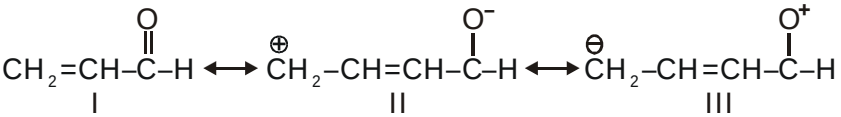


Example 17.

Write resonance structures of $CH_2 = CH - CHO$. Indicate relative stability of the contributing structures.

Strategy.

Resonating structure of CH_2=CH–CHO will be



Relative stability of resonating structures are judged by generally these following points.

(A) Neutral molecules are generally more stable than charged.

(B) Greater the number of π bond, greater will be the stability.

(C) Structure with complete octet for each atom is generally more stable than those in which atleast one atom have incomplete octet.

(D) Structures with negative charge on electronegative atom & positive charge on electropositive atom is more stable than those in which electronegative atom have positive charge & electropositive atom have negative charge.

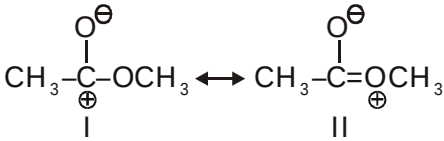
(E) Two similar charge present neares to each other creates electronic repulsion which destabilize the molecule but two dissimilar charge present nearer to each other creates electronic attraction and stabilize the molecule.

(F) Resonating structure with linear conjugation is more stable than structure with cross conjugation.

So relative stability of resonating structures of CH_2=CH–CHO will be I > II > III.

Example 18.

Explain why the following two structures, I and II cannot be the major contributors to the real structure of CH_3COOCH_3.



Strategy.

I[st] structure is less contributor as it has atom with incomplete octet while II[nd] structure is less contributor because of charge separation of positive & negative charge.

Example 19.

Explain why $(CH_3)_3\overset{+}{C}$ is more stable than $CH_3\overset{+}{C}H_2$ and $\overset{+}{C}H_3$ is the least stable cation.

Strategy.

Stability of carbocation is generally decided by electronic effect such as resonance, hyperconjugation & inductive effect. Greater is the positive electronic effects, greater is the stability. So,

$$\underset{9\,HC}{(CH_3)_3C^{\oplus}} > \underset{3\,HC}{CH_3\overset{\oplus}{C}H_2} > \underset{0\,HC}{CH_3^{\oplus}}$$

Example 20.

On complete combustion, 0.246g of an organic compound gave 0.198g of carbon dioxide and 0.1014g of water. Determine the percentage composition of carbon and hydrogen in the compound.

Strategy.

% composition of C & H in compound will be

$$\%\text{ of C} = \frac{12 \times \text{mass of } CO_2 \times 100}{44 \times \text{mass of compound}}$$

$$\%\text{ of H} = \frac{2 \times \text{mass of water} \times 100}{18 \times \text{mass of compound}}$$

$$\Rightarrow \quad \%\text{ of C} = \frac{12 \times 0.198 \times 100}{44 \times 0.246} = 21.95\%$$

$$\%\text{ of H} = \frac{2 \times 0.1014 \times 100}{18 \times 0.246} = 4.58\%$$

Example 21.

In Dumas' method for estimation of nitrogen, 0.3g of an organic compound gave 50mL of nitrogen collected at 300K temperature and 715mm pressure.

Strategy.

Volume of nitrogen collected at 300K and 715 mm pressure is 50 ml.

Actual pressure = 715 – 15 = 700 mm

Volume of nitrogen at STP $= \frac{273 \times 700 \times 50}{300 \times 760} = 41.9$ mL

22,400 mL of N_2 at STP weighs = 28g

41.9 mL of nitrogen weighs $= \frac{28 \times 41.9}{22400}$ g

% of nitrogen $= \frac{28 \times 41.9 \times 100}{22400 \times 0.3} = 17.46\%$

Example 22.

During estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5g of the compound in Kjeldahl's estimation of nitrogen, neutralized 10mL of 1 M H_2SO_4. Find out the percentage of nitrogen in the compound.

Strategy.

1M of 10mL $H_2SO_4 = 1$M of 20mL NH_3

1000mL of 1M NH_3 contains 14g N

20mL of 1M NH_3 contain $\frac{14 \times 20}{1000}$ g N

So % of N $= \frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0\%$

Example 23.

In Carius method of estimation of halogen, 0.15g of an organic compound gave 0.12 g of AgBr. Find out the percentage of bromine in the compound.

Strategy.

Molar mass of AgBr = 108 + 80 = 188 g/mol

188 g AgBr contains 80 g Br

So 0.12 g AgBr contains $\frac{80 \times 0.12}{188}$ g Br

Hence, % of Br $= \frac{80 \times 0.12 \times 100}{188 \times 0.15} = 34.04\%$

Example 24.

In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound?

Strategy.

Molecular mass of $BaSO_4$ = 137 + 32 + 64 = 233 g

233 g $BaSO_4$ contains 32 g S

So, 0.4813 g $BaSO_4$ contains $\frac{32 \times 0.4813}{233}$ g S

% of S $= \frac{32 \times 0.4813 \times 100}{233 \times 0.157} = 42.10\%$

❑ ❑ ❑

Exercise Problems:

Exercise Problem 1.

What are hybridisation states of each carbon atom in the following compounds?

$CH_2 = C = O, CH_3CH = CH_2, (CH_3)_2CO, CH_2 = CHCN, C_6H_6$

Strategy.

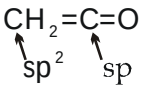
To write the hybridization of any atom, always count the number of σ bond & lp of e^-. If

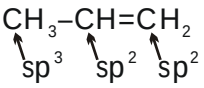
Sum of σ bond + lp = 2 $\Rightarrow$ sp hybridization

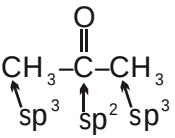
Sum of σ bond + lp = 3 $\Rightarrow$ sp^2 hybridization

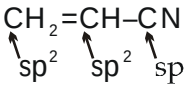
Sum of σ bond + lp = 4 $\Rightarrow$ sp^3 hybridization

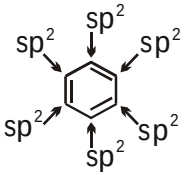
So hybridization state of each carbon atom will be











Exercise Problem 2.

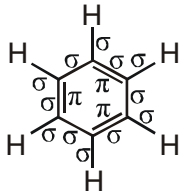
Indicate the σ and π bonds in the following molecules :

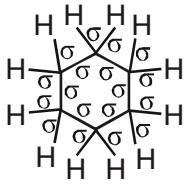
$C_6H_6, C_6H_{12}, CH_2Cl_2, CH_2 = C = CH_2, CH_3NO_2, HCONHCH_3$

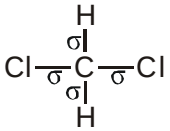
Strategy.

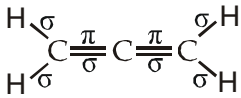
To find total number of σ & π bonds present in any molecule, first expand the molecule and then look for single, double & triple bond. Single bond are only σ bond, double bond have

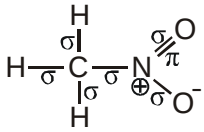
1σ & 1π bond while triple bond have 1σ & 1π bonds.

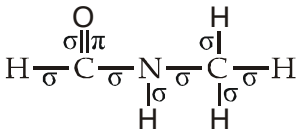












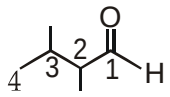
Exercise Problem 3.

Write bond line formulas for : Isopropyl alcohol, 2,3-Dimethyl butanal, Heptan-4-one.

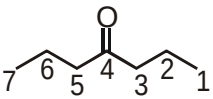
Strategy.

To draw bond line formulas of any compound, first draw the skelelon of carbon taking the help of word root of IUPAC nomenclature & then add substituent or functional group on appropriate position in it.

Iso-propyl alcohol



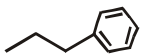
2,3-Dimethylbutanal

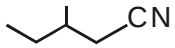


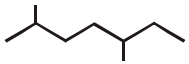
Heptan-4-one

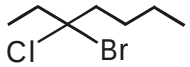
Exercise Problem 4.

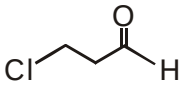
Give the IUPAC names of the following compounds :

(A) 

(B) 

(C) 

(D) 

(E) 

(F) Cl_2CHCH_2OH

Strategy.

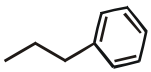
To write the IUPAC name of any compound, always use

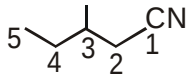
(A) 2°prefix + 1°prefix + word root + 1°suffix + 2°suffix in sequence.

(B) Use the concept of position then alphabet then position if functional group, multiple bond or substituents are present.

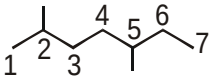
(C) For giving minimum position- Functional group- multiple bond- Substituent.

(D) If more than one functional groups are present, then use the concept of priority order.

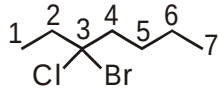
(A) 
Propylbenzene

(B) 

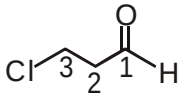
3-Methylpentane nitrile

(C) 

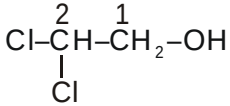
2,5-Dimethylheptane

(D) 

3-Bromo-3-chloroheptane

(E) 

3-Chloropropanal

(F) 

2,2-Dichloroethanol

Exercise Problem 5.

Which of the following represents the correct IUPAC name of the compounds concerned ?

(A) 2,2-Dimethylpentane or 2-Dimethylpentane

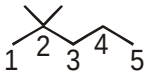
(B) 2,4,7-Trimethyloctane or 2,5,7-Trimethyloctane

(C) 2-Chloro-4-methylpentane or 4-Chloro-2-methylpentane

(D) But-3-yn-1-ol or But-4-ol-1-yne.

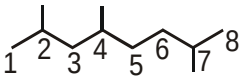
Strategy.

To solve such questions, first draw the incorrect structures from given IUPAC name taking the help of word root of IUPAC & the correct it using main above concept.



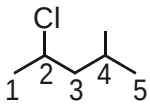
(A) 2,2-Dimethylpentane (correct)
2-Dimethylpentane (incorrect)

If more than one substituents are present in molecule, then indicate the position of each substituent.



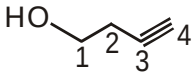
(B) 2,4,7-Trimethyloctane (correct)
2,5,7-Trimethyloctane (incorrect)

Always place the substituents at minimum position.



(C) 2-Chloro-4-methylpentane (correct)
4-Chloro-2-methylpentane (incorrect)

If position of substituents are same from both end, then substituent with lower alphabet are given lower position.



(D) But-3-yn-1-ol (correct)
But-4-ol-1-yne (incorrect)

If compound have functional group as well as multiple bond then functional group is given lower position.

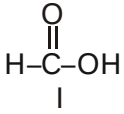
Exercise Problem 6.

Draw formulas for the first five members of each homologous series beginning with the following compounds.

(A) $H-COOH$ (B) CH_3COCH_3 (C) $H-CH=CH_2$

Strategy.

(A) First five member of H–COOH will be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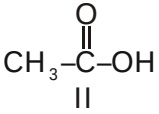
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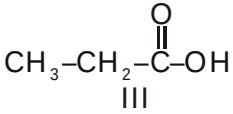
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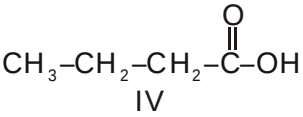
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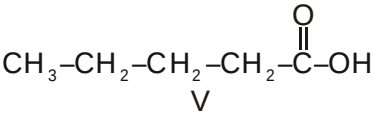
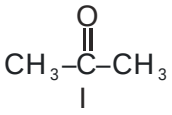

V

(B) First five member of CH_3COCH_3 will be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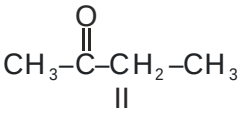
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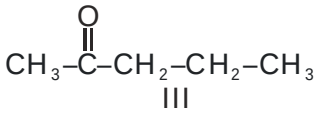
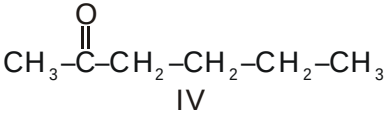

III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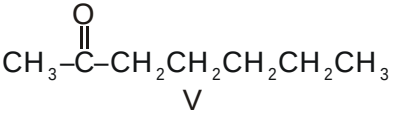
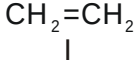

V

(C) First five member of $H-CH=CH_2$ will be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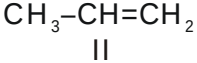
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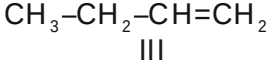
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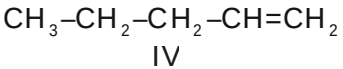
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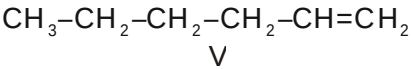

V

Exercise Problem 7.

Give condensed and bond line structural formulas and identify the functional group(s) present, if any, for :

(A) 2,2,4-Trimethylpentane

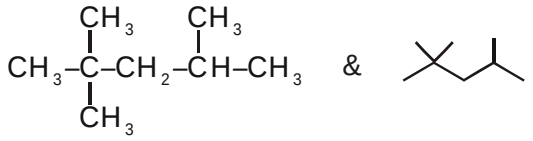
(B) 2-Hydroxy-1,2,3-propanetricarboxylic acid

(C) Hexanedial

Strategy.

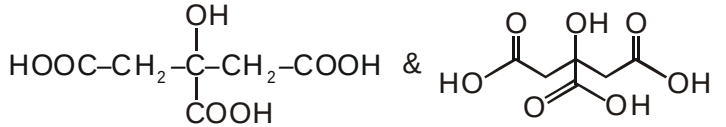
The condensed & bond line formula of any compound can be drawn by taking the help of word root.

(A)



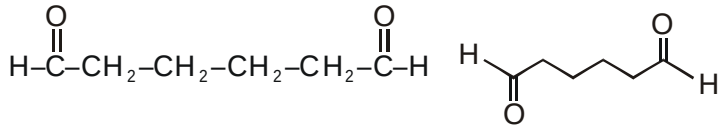
2,2,4-Trimethylpentane

(B)



2-Hydroxy-1,2,3-propanetricarboxylic acid

(C)

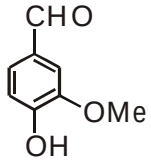


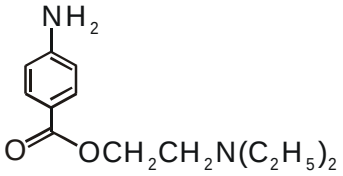
Hexanedial

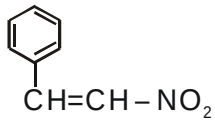
Functional group present in (B) are alcohol & carboxylic acid & (C) is aldehyde while (A) do not have any functional group.

Exercise Problem 8.

Identify the functional groups in the following compounds

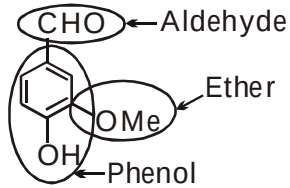
(A) 

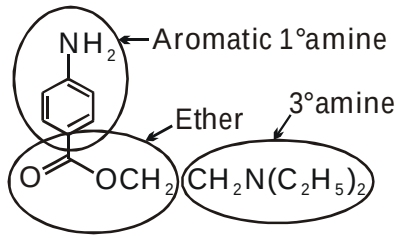
(B) 

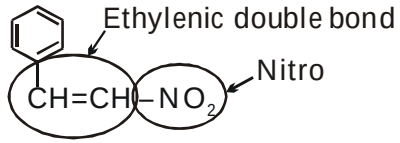
(C) 

Strategy.

Functional groups present in following compounds are

(A) 

(B) 

(C) 

Exercise Problem 9.

Which of the two: $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ is expected to be more stable and why ?

Strategy.

Stability of any molecule depends on the dispersion of electron density. Greater is the dispersion of charge, greater is the stability. So,

$O_2N–CH_2–CH_2–O^-$ is more stable than $CH_3–CH_2–O^-$ because $–NO_2$ group withdraws electron density by –I effect in first which disperses –ve charge while $–CH_3$ group donates electron density by +I effect which intensity the negative charge.

$O_2N \leftarrow CH_2 \leftarrow CH_2 \leftarrow O^-$ (more stable)

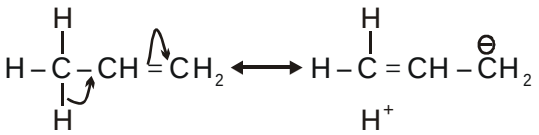
$CH_3 \rightarrow CH_2 \leftarrow O^-$ (less stable)

Exercise Problem 10.

Explain why alkyl groups act as electron donors when attached to a π system.

Strategy.

Alkyl groups acts as electron donors when attached to a π bonded system of C=C bond because of hyperconjugation. In this electronic effect C–H sigma bond overlap with adjacent π bond.



(Propene)

Exercise Problem 11.

Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.

(A) C_6H_5OH (B) $C_6H_5NO_2$

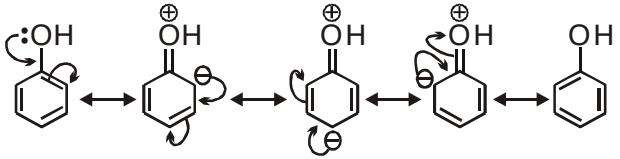
(C) $CH_3CH=CHCHO$ (D) C_6H_5-CHO

(E) $C_6H_5-\overset{\oplus}{C}H_2$ (F) $CH_3CH=CH\overset{\oplus}{C}H_2$

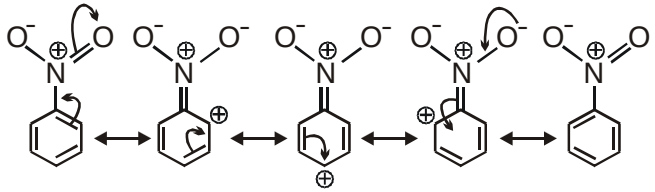
Strategy.

To write resonating structure of any molecule, first write the structure of it and then put unshared electron or charge if present on appropriate atom & then draw arrow one at a time by moving the electrons to get other structures.

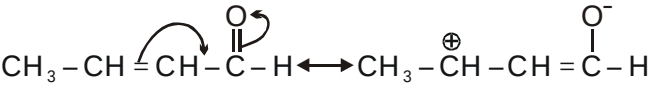
(A)



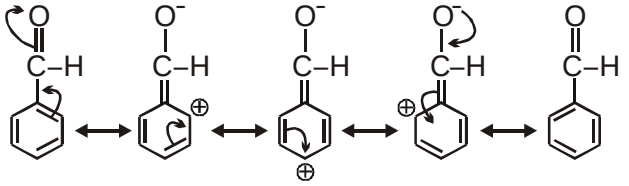
(B)



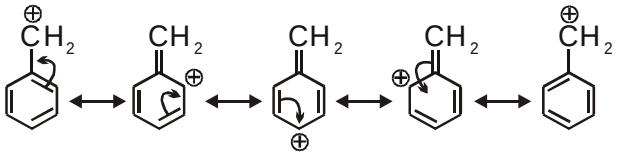
(C)



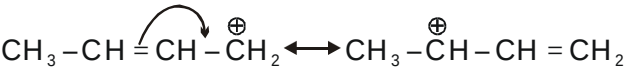
(D)



(E)



(F)



Exercise Problem 12.

What are electrophiles and nucleophiles ? Explain with examples.

Strategy.

Electrophile- They are the electron deficient species which have capacity to accept a pair of e^-. This electron deficiency may be of seen as

(A) Positive charge such as H^+, Cl^+, Br^+, NO_2^+, NO^+, R^+, RCO^+ etc.

(B) Incomplete octet such as BF_3, $AlCl_3$.

(C) Vacant orbital- Such as $FeCl_3$, $SiCl_4$, $SbCl_5$ etc.

Nucleophile- They are electron rich species which have capability to donate a pair of e^-. They have either –ve charge or have lone pair of electrons with complete octet.

(A) Negative charge- Such as X^-, OH^-, $\overset{\ominus}{N}H_2$, $\overset{\ominus}{O}R$ etc.

(B) Lone pair of e^-- Such as NH_3, H_2O, CH_3OH etc.

Exercise Problem 13.

Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles:

(A) $CH_3COOH + \mathbf{HO^-} \rightarrow CH_3COO^- + H_2O$

(B) $CH_3COCH_3 + \mathbf{\bar{C}N} \rightarrow (CH_3)_2C(CN)(OH)$

(C) $C_6H_5 + CH_3\overset{+}{C}O \rightarrow C_6H_5COCH_3$

Strategy.

As stated above nucleophiles are electron rich species with either –ve charge or with lone pair of electrons with complete octct, while electrophiles are electron deficient species with either positive charge, vacant orbital or incomplete octct. So,

(A) $CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$

(Nucleophile but acts as a base)

(B) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + \overset{\ominus}{CN} \longrightarrow CH_3-\underset{\underset{CN}{|}}{\overset{\overset{O^-}{|}}{C}}-CH_3 \xrightarrow{H^+} CH_3-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$

(Nucleophile)

(C) $+ CH_3-\overset{\overset{O}{\|}}{C}\oplus \longrightarrow$

(Electrophile)

Exercise Problem 14.

Classify the following reactions in one of the reaction type studied in this unit.

(A) $CH_3CH_2Br + HS^- \rightarrow CH_3CH_2SH + Br^-$

(B) $(CH_3)_2C = CH_2 + HCl \rightarrow (CH_3)_2ClC - CH_3$

(C) $CH_3CH_2Br + HO^- \rightarrow CH_2 = CH_2 + H_2O + Br^-$

(D) $(CH_3)_3C - CH_2OH + HBr \rightarrow (CH_3)_2CBrCH_2CH_2CH_3 + H_2O$

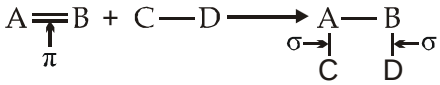
Strategy.

Organic reactions are mainly of 4 types-

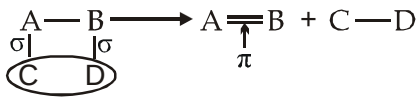
(A) **Substitution reaction-** Here generally sigma bonds are broken & corresponding new sigma bonds are formed.

$A\underset{\sigma}{-}B + C \longrightarrow A\underset{\sigma}{-}C + B$

(B) **Addition reaction-** Here generally pi bonds are broken & corresponding 2 new sigma bonds are formed.



(C) **Elimination reaction-** Here generally sigma bonds are broken & corresponding new pi bonds are formed.



(D) **Rearrangement reaction-** Here generally attachment of atom changes in carbon skeleton of substrate.

On the basis of first attack of reagent, substitution reaction is of further 3 types.

(A) Nucleophilic substitution reaction

(B) Electrophilic substitution reaction

(C) Free radical substitution reaction

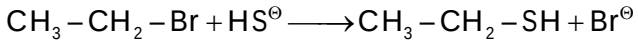
On the basis of first attack of reagent, addition reaction is also of further 3 types.

(A) Nucleophilic addition

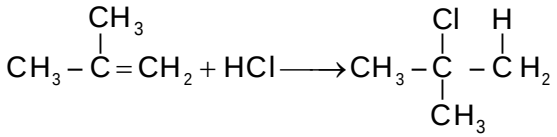
(B) Electrophilic addition

(C) Free radical addition

So,

(A) 

Here σ bond is broken & new σ bond is formed by attack of a nucleophile so reaction is nucleophilic substitution reaction.

(B) 

Here π bonds are broken & corresponding 2 new sigma bonds

are formed by attack of an electrophile so reaction is electrophilic addition reaction.

(C) $CH_3-CH_2-Br+O\overset{\ominus}{H}\longrightarrow CH_2=CH_2+H_2O+Br^{\ominus}$

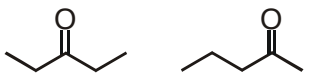
In this reaction 2 sigma bonds are broken & corresponding a pi bond is formed, so reaction is elimination reaction.

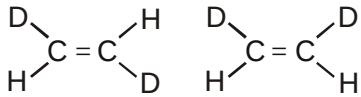
(D) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2OH+HBr\rightarrow CH_3-\underset{\displaystyle Br}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2CH_3+H_2O$

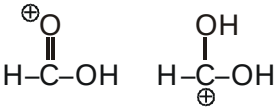
Here again σ bond is broken and corresponding new σ bond is formed by attack of a nucleophile & reaction follows nucleophilic substitution reaction, but as position of methyl group change in substrate to product, so rearrangement reaction is also seen along with nucleophilic substitution reaction.

Exercise Problem 15.

What is the relationship between the members of following pairs of structures ? Are they structural or geometrical isomers or resonance contributors?

(A) 

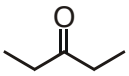
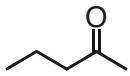
(B) 

(C) 

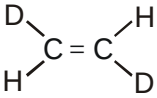
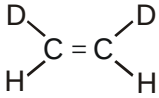
Strategy.

To find out structural & stereo isomers, always think for the IUPAC name. If IUPAC of isomers are different they are streuctural isomers but if they have same IUPAC name, then they are stereoisomers.

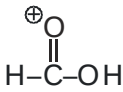
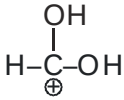
To find out resonating structure, always look for the position of bonding π electron & non-bonding electron as position of atoms remains same in all resonating structures.

(A)  Pentan-3-one  Pentan-2-one

As they have different IUPAC name, so are structural isomers.

(B)  Trans-1,2-Deuteroethene  Cis-1,2-Deuteroethene

As they have same IUPAC name but the spacial arrangement of deuterium along C=C double bond is different, so are geometrical isomers.

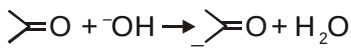
(C)  

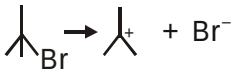
As position of atoms are same but have difference in position of π electrons, so are resonating structures.

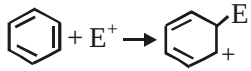
Exercise Problem 16.

For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion.

(A) $CH_3O-OCH_3 \rightarrow CH_3\dot{O} + \dot{O}CH_3$

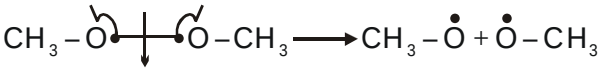
(B) 

(C) 

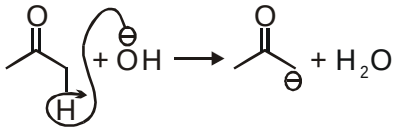
(D) 

Strategy.

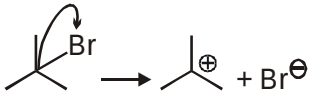
The following reaction follows

(A) 

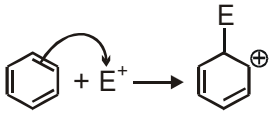
Here sigma bond is broken homolytically to form free radicals.

(B) 

Here base abstract proton heterolytically to form carbanion as a reaction intermediate.

(C) 

Here C–Br bond is broken heterolytically to form carbocation as a reaction intermediate.

(D) 

Here benzene attacks over an electrophile heterolytically to form carbocation as a reaction intermediate.

Exercise Problem 17.

Explain the terms inductive and Electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?

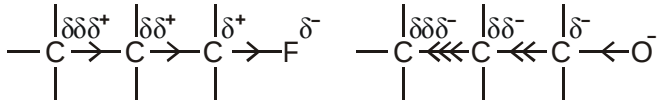
(A) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

(B) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$

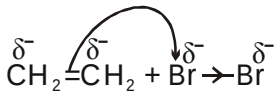
Strategy.

Inductive effect- It is a permanent displacement of electron density along sigma bond and transmit along the carbon chain

when two atom have electronegativity difference. This transmission of polarity along σ bond is called as Inductive effect.



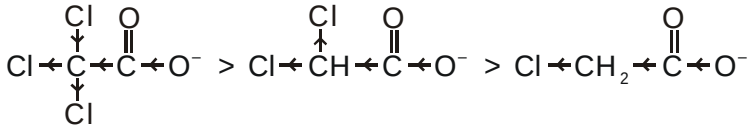
Electromeric effect- It is a temporary displacement of π electron density in carbon carbon multiple bond when a reagent attacks over the substrate.



Acidic character of any molecule depends on the stability of conjugate base, so in both the cases inductive effect explains the relative stability of conjugate base & acidic strength follows

(A) $Cl_3C–COOH > Cl_2CH–COOH > ClCH_2–COOH$

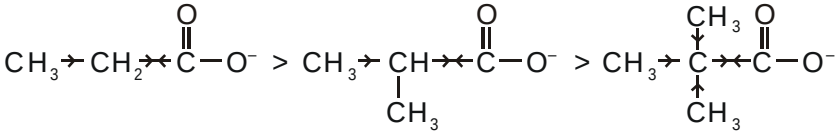
The stability of conjugate base follows



(3-I of Cl) (2-I of Cl) (1-I of Cl)

(B) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$

The stability of conjugate base follows



(Repulsion with 1 CH_3 group) (Repulsion with 2 CH_3 group) (Repulsion with 3 CH_3 group)

Exercise Problem 18.

Give a brief description of the principles of the following techniques taking an example in each case.

(A) Crystallisation (B) Distillation (C) Chromatography

Strategy.

(A) **Crystallisation-** In this process we convert an impure compound into a pure crystals. This process is based on the difference in the solubility of the compound and the impurities in a suitable solvent. Here the impure compound is dissolved in a solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperature.

Now solution is concentrated to get a nearly saturated solution at higher temperature. On cooling the solution, pure compound in the form of crystals separates.

The best example of crystallisation is iodoform crystallisation with alcohol & benzoic acid mixed with naphthalene be purified by not water.

(B) **Distillation-** Distillation involves the process of heating a liquid to convert it into the vapour and then condensing the vapour to get back to the liquid.

This process of separation is applied only for the purification of liquid which boil without decomposition at atmospheric pressure and contain non-volatile impurities. So mixture of two liquids having sufficient difference in their boiling points can be separated and purified by this process.

The best example are the separation of chloroform (bp 334K) & aniline (bp 457K) can be done by it.

(C) **Chromatography-** It is a technique for the separation, purification & identification of constituents of mixtures. Chromatography is based on the principle of selective adsorption of components of a mixture between two phase i.e. a stationary phase and a moving phase. Here the

stationary phase can be a solid or a liquid while moving phase is generally liquid or gas.

Exercise Problem 19.

Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.

Strategy.

Two compounds with different solubilities is a solvent S can be separated by the method called as **Fractional crystallisation**.

In this process, a hot saturated solution of these two compounds is allowed to cool, the less soluble compound crystalises out earlier than the more soluble compound. Now the crystals are separated from the mother liquor & the mother liquor is again concentrated and allowed to cool, then the crystal of the second compound is obtained.

Exercise Problem 20.

What is the difference between distillation, distillation under reduced pressure and steam distillation ?

Strategy.

This question is based on separation of compounds having difference in boiling point. Distillation simply involves the process of heating liquid to convert it into the vapours and the condensation of the vapours to get back the liquid.

- ✓ **Simple distillation** is applied only for purification of those liquids which boil without decomposition and contains non-volatile impurities.
- ✓ **Distillation under reduced pressure** is applied for those organic liquids which decomposes at a temperature below their boiling point.
- ✓ **Steam distillation** is simply co-distillation with water. This technique is used to separate substance which are steam volatile and are immiscible with water.

Exercise Problem 21.

Discuss the chemistry of Lassaigne's test.

Strategy.

Chemistry of Lassaigne's test- Organic compounds are covalently bonded so they are first converted to ions by fusing with sodium at high temperature, then only we can test the presence of perticular element in compound.

In this process we first prepare sodium extract & then test the presence of elements.

Preparation of sodium extract- Here organic compounds are first fused with sodium and heated upto red hot in ignition tube. Then we broke the red hot ignition tube in water & filter the solution. The filterate obtained on this is called as sodium extract. Now this sodium extract can be used to detect the presence of N, S, X in organic compound.

Test of Nitrogen- Here sodium extract is treated with ferrous sulphate. If prussian blue colour is obtained, then compound have presence of N.

$$Na + C + N \longrightarrow NaCN$$

$$FeSO_4 + 2NaOH \longrightarrow \underset{\text{Ferrous hydroxide (green)}}{Fe(OH)_2} + Na_2SO_4$$

$$Fe(OH)_2 + 6NaCN \longrightarrow \underset{\text{Sodium ferrocyanide}}{Na_4[Fe(CN)_6]} + 2\,NaOH$$

On heating some Fe^{2+} ions are oxidized to Fe^{3+} ion

$$4Fe^{3+} + 3Na_4[Fe(CN)_6] \longrightarrow \underset{\text{Ferric ferrocyanide (Prussian blue)}}{Fe_4[Fe(CN)_6]_3} + 12\,Na^+$$

Test of Nitrogen & Sulphur if present together.

$$Na + C + N + S \longrightarrow \underset{\text{Sodium thiocyanate}}{NaSCN}$$

$$Fe^{3+} + NaSCN \longrightarrow \underset{\text{Blook red colour}}{Fe(SCN)_3} + 3Na^+$$

Test of sulphur- Here sodium extract is treated with lead acetate. If black ppt is obtained, then compound have presence of S.

$$Na + S \longrightarrow Na_2S$$

$$Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{(Black ppt)}}{PbS} + 2CH_3COONa$$

There is one more test of sulphur. Here sodium extract is treated with sodium nitroprusside solution. If a violet colour ppt is obtained, then compound have presence of S.

$$Na_2S + Na_2[Fe(NO)(CN)_5] \longrightarrow \underset{\substack{\text{Sodium thionitroprusside}\\ \text{(violet ppt)}}}{Na_4[Fe(CN)_5NOS]}$$

Test of halogen- Before testing halogens, sodium extract is boiled with conc. HNO_3 to decompose sodium cyanide or sodium sulphide in the sodium extract, otherwise these ions would interfere with silver nitrate test for halogen.

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN\uparrow$$

$$Na_2S + HNO_3 \longrightarrow NaNO_3 + H_2S\uparrow$$

Now add $AgNO_3$ to sodium extract. If white precipitate is obtained which is soluble in ammonium hydroxide but insoluble in HNO_3, then it indicates the presence of –Cl.

$$NaCl + AgNO_3 \longrightarrow \underset{\text{White ppt}}{AgCl\downarrow} + NaNO_3$$

If pole yellow ppt is obtained which is sparingly soluble in ammonium hydroxide, then it indicate the presence of –Br.

$$NaBr + AgNO_3 \longrightarrow \underset{\text{Pole yellow ppt}}{AgBr\downarrow} + NaNO_3$$

If yellow ppt is obtained which is insoluble in ammonium hydroxide, then it indicates the presence of iodine.

$$NaI + AgNO_3 \longrightarrow \underset{\text{yellow ppt}}{AgI} + NaNO_3$$

Exercise Problem 22.

Differentiate between the principle of estimation of nitrogen in an organic compound by (i) Dumas method and (ii) Kjeldahl's method.

Strategy.

Dumas method- Here a known mass of the nitrogen containing organic compound is heated with excess of CuO in an atmosphere of CO_2, then nitrogen of organic compound is converted into N_2 gas. So the volume of N_2 gas thus obtained is converted into STP and the % of nitrogen can be determined.

$$\% \ N = \frac{28}{22400} \times \frac{\text{Volume of } N_2 \text{ at STP}}{\text{Mass of the substance taken}} \times 100$$

Kjeldahl's method- Here a known mass of the nitrogen containing organic compound is heated with excess of conc. H_2SO_4 in presence of $CuSO_4$ in Kjeldahl's flask, then nitrogen of organic compound is converted into $(NH_4)_2SO_4$. This ammonium sulphate is then boiled with excess of NaOH solution to liberate NH_3 gas which is absorbed in a known excess of standard solution of H_2SO_4 or HCl.

The volume of acid left after absorption of ammonia is estimated by titration against a standard alkaline solution. From the volume of the acid used, the percentage of nitrogen is determined by applying the mathermatical equation.

$$\% \ N = \frac{1.4 \times \text{Molarity of acid} \times \text{basicity of acid} \times \text{vol. of acid}}{\text{Mass of substance taken}}$$

Exercise Problem 23.

Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound.

Strategy.

Principle of estimation of halogens- Here a known mass of an organic compound is heated with fuming HNO_3 in the

presence of $AgNO_3$ in Carius tube in a furnace. By doing so, carbon & hydrogen present in the organic compounds are oxidised to CO_2 and H_2O respectively and halogen forms the precipitate of AgX. Now this AgX is filtered, washed, dried & weighed. So,

$$\% \text{ of halogen} = \frac{\text{Atomic mass of X x mass of AgX} \times 100}{\text{Molecular mass of AgX} \times \text{mass of compound}}$$

Principle of estimation of sulphur- Here a known mass of an organic compound is heated with Carius tube with sodium peroxide on fuming HNO_3. By doing so, sulphur is oxidised to H_2SO_4 and precipitated as $BaSO_4$ by adding excess of $BaCl_2$ solution in water. Now this $BaSO_4$ is filtered, washed, dried & weighed.

$$\% \text{ of S} = \frac{32 \times \text{Mass of } BaSO_4 \times 100}{233 \times \text{Mass of compound}}$$

Principle of estimation of phosphorus- Here a known mass of an organic compounds is heated with fuming HNO_3. By doing so, phosphorus is oxidised to phosphoric acid and precipitated as ammonium phosphomolybdate $(NH_4)_3PO_4.12\,MoO_3$ by adding NH_3 and ammonium phosphomolybdate. Now $(NH_4)_3PO_4.12\,MoO_3$ is filtered, washed, dried & weighed.

$$\% \text{ of P} = \frac{31 \times \text{Mass of ammonium molybdate} \times 100}{1877 \times \text{Mass of organic compound}}$$

Exercise Problem 24.

Explain the principle of paper chromatography.

Strategy.

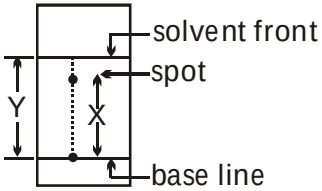
Principle of paper chromatography- It is a type of partition chromatography & based on principle of partition i.e. based on continuous differential distribution of the various components of the mixture between the stationary and the

mobile phases.

In this process, the solution of the mixture which is to be separated is applied as a small spot at the base of chromatography paper nearly 2cm above one end of the paper strip. Now this paper is suspended in a suitable solvent. This solvent acts as mobile phase due to which solvent rises up the paper.

After some time the spots of the separated coloured compounds are visible at different heights from the position of inital spot on the chromatogram.

The coloured components of a mixture are identified by Retardation factor, R_f value, which is fix value for every component.



Observation on paper chromatograph

$$R_f \text{ value} = \frac{\text{Distance travelled by the compound (X)}}{\text{Distance travelled by the solvent (Y)}}$$

Exercise Problem 25.

Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?

Strategy.

Conc. HNO_3 is added to sodium extract before adding silver nitrate before testing halogen is to remove NaCN or Na_2S if present in sodium extract, otherwise they give white ppt & black ppt with $AgNO_3$ which creats confusion.

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN\uparrow$$

$$Na_2S + HNO_3 \longrightarrow NaNO_3 + H_2S\uparrow$$

otherwise

$$NaCN + AgNO_3 \longrightarrow \underset{\text{White ppt}}{AgCN} + NaNO_3$$

$$Na_2S + AgNO_3 \longrightarrow \underset{\text{(Black ppt)}}{Ag_2S} + NaNO_3$$

Exercise Problem 26.

Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens.

Strategy.

Organic compounds are covalently bonded so the detection of element is not easy so, they are first fused with sodium to convert them into ion, which we get by easy chemical test.

$$Na + C + N \longrightarrow NaCN$$

$$Na + S \longrightarrow Na_2S$$

$$Na + X \longrightarrow NaX$$

Exercise Problem 27.

Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

Strategy.

Suitable technique used for separation of components from mixture of calcium sulphate & comphor is **sublimation**.

As camphor is sublimable but $CaSO_4$ is not so sublimation of the mixture gives camphor on the side of funnel while $CaSO_4$ is left in the china dish.

Exercise Problem 28.

Explain, why an organic liquid vaporises at a temperature below its boiling point in its steam distillation ?

Strategy.

In steam distillation process, the mixture consisting of the organic liquid and water boils when the sum of the vapour

pressure of the organic liquid and that of water becomes equal to the atmospheric pressure.

Atmospheric pressure = Vapour pressure of the liquid + Vapour pressure of the water.

Since, vapour pressure of the liquid is lower than atmospheric pressure, the organic liquid vaporises at lower temperature than its boiling point.

Exercise Problem 29.

Will CCl_4 give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer.

Strategy.

No, CCl_4 will not give white precipitate of AgCl on heating with $AgNO_3$ because CCl_4 is covalently bonded compound and will not ionize to give Cl^- ion required for the formation of AgCl as precipitate.

Exercise Problem 30.

Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?

Strategy.

As carbon dioxide is slightly acidic in nature, therefore it will react with strong base like KOH to form K_2CO_3 & from the weight of CO_2 obtained, % of carbon in the organic compound can be calculated.

$$KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

$$\% \text{ of } C = \frac{12 \times \text{weight of } CO_2 \text{ formed}}{\text{Weight of substance taken}} \times 100$$

Exercise Problem 31.

Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

Strategy.

When H_2SO_4 is used for acidification of sodium extract for testing sulphur by lead acetate test, then lead acetate itself react with H_2SO_4 to form white ppt of lead sulphate.

$$(CH_3COO)_2Pb + H_2SO_4 \longrightarrow \underset{\text{White ppt}}{PbSO_4\downarrow} + CH_3COOH$$

Hence, this white ppt of $PbSO_4$ will interfere with the following test of sulphur.

$$(CH_3COO)_2Pb + NaS \longrightarrow \underset{\text{Black ppt}}{PbS\downarrow} + CH_3COONa$$

However, if acetic acid is used, it does not react with lead acetate, so it will not interfere in the test.

Exercise Problem 32.

An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.

Strategy.

Calculation of mass can be done by following formula.

$$\% \text{ of } C = \frac{12 \times \text{Mass of } CO_2 \text{ formed}}{44 \times \text{mass of substance taken}} \times 100$$

$$69 = \frac{12 \times \text{Mass of } CO_2 \text{ formed}}{0.2} \times 100$$

So, mass of CO_2 formed = 0.506 gram.

$$\% \text{ of } H = \frac{2 \times \text{Mass of } H_2O \text{ formed}}{\text{Mass of substance taken}} \times 100$$

$$4.8 = \frac{2 \times \text{Mass of } H_2O \text{ formed}}{18 \times 0.2} \times 100$$

So, mass of H_2O formed = 0.0864 g.

Exercise Problem 33.

A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50ml of 0.5 M H_2SO_4. The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.

Strategy.

Volume of H_2SO_4 taken = 50 mL of 0.5 M H_2SO_4

= 25 mL of 1.0 M H_2SO_4

Volume of alkali used for neutralization of excess acid

= 60 mL of 0.5 M NaOH

= 30 mL of 1.0 M NaOH

As, $H_2SO_4 + 2\,NaOH \longrightarrow Na_2SO_4 + 2\,H_2O$

So, 1 mole of H_2SO_4 = 2 mole of NaOH

Hence, 30 mL of 1.0 M NaOH = 15 mL of 1.0 M H_2SO_4

$\therefore$ Volume of acid used by ammonia = 25–15 = 10 mL

$\therefore$ $$\%\text{ of Nitrogen} = \frac{1.4 \times N_1 \times \text{Vol. of acid used}}{\text{Mass of organic compound}}$$

$$\%\text{ of Nitrogen} = \frac{1.4 \times 2 \times 10}{0.5} = 56.0$$

Exercise Problem 34.

0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound.

Strategy.

Mass of organic compound taken = 0.3780 g.

Mass of AgCl formed = 0.5740 g.

$$\% \text{ of Cl} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl formed}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{35.5}{143.5} \times \frac{0.5740}{0.3780} \times 100 = 37.566\%$$

Exercise Problem 35.

In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find out the percentage of sulphur in the given compound.

Strategy.

Mass of organic compound taken = 0.468 g.

Mass of $BaSO_4$ formed = 0.668 g.

$$\% \text{ of S} = \frac{32}{233} \times \frac{\text{Mass of } BaSO_4 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{32}{233} \times \frac{0.668}{0.468} \times 100 = 19.60\%$$

Exercise Problem 36.

In the organic compound $CH_2 = CH - CH_2 - CH_2 - C \equiv CH$, the pair of hydridised orbitals involved in the formation of : $C_2 - C_3$ bond is:

(A) $sp - sp^2$ (B) $sp - sp^3$

(C) $sp^2 - sp^3$ (D) $sp^3 - sp^3$

Strategy.

To find out hybridised orbital first write hybridization of each carbon & then report your answer.

So, hybridised orbitals involved in the formation of C_2–C_3 bond is sp^2–sp^3.

Exercise Problem 37.

In the Lassaigne's test of nitrogen in an organic compound, the Prussian blue colour is obtained due to the formation of :

(A) $Na_4[Fe(CN)_6]$ (B) $Fe_4[Fe(CN)_6]_3$

(C) $Fe_2[Fe(CN)_6]$ (D) $Fe_3[Fe(CN)_6]_4$

Strategy.

In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue colour is obtained due to formation of $Fe_4[Fe(CN)_6]_3$.

$$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$

$$Fe(OH)_2 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$$

$$4Fe^{3+} + 3Na_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6]_3 + 12Na^+$$

Exercise Problem 38.

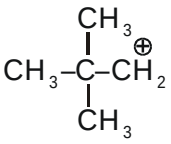
Which of the following carbocation is most stable ?

(A) $(CH_3)_3C.\overset{+}{C}H_2$ (B) $(CH_3)_3C^+$

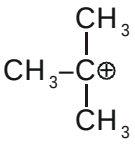
(C) $CH_3CH_2\overset{+}{C}H_2$ (D) $CH_3\overset{+}{C}HCH_2CH_3$

Strategy.

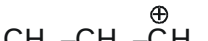
Greater is the number of hyperconjugating structure, greater is the stability of carbocation. So $(CH_3)_3C^+$ is most stable carbocation.



(0 HC)



(9 HC)



(2 HC)

(5 HC)

Exercise Problem 39.

The best and latest technique for isolation, purification and separation of organic compounds is :

(A) Crystallisation (B) Distillation

(C) Sublimation (D) Chromatography

Strategy.

The best & latest technique for isolation, purification & separation of organic compound is chromatography.

Exercise Problem 40.

The reaction :

$$CH_3CH_2I + KOH(aq) \rightarrow CH_3CH_2OH + KI$$

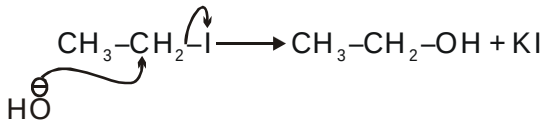
is classified as :

(A) electrophilic substitution (B) nucleophilic substitution

(C) elimination (D) addition

Strategy.

The reaction is classified as nucleophilic substitution reaction as nucleophile (OH^-) attacks over carbon directly attached to I to replace it with itself.



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