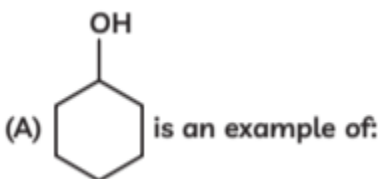


# Organic Chemistry-Some Basic Principles and Techniques

## Case Study Based Questions

Read the following passages and answer the questions that follow:

1. Alicyclic compounds (aliphatic cyclic) are made up of carbon atoms arranged in a ring (homocyclic). Other atoms than carbon are known to exist in the ring (heterocyclic). A heterocyclic compound is an organic compound in which one or more of the carbon atoms in the backbone of the molecule has been replaced by an atom other than carbon. Some of its properties are similar to those of aliphatic compounds. Aromatic compounds are a class of chemicals. Examples include benzene and other similar ring compounds (benzenoid). Benzenoid compounds contain at least one benzene ring in the molecule whereas non benzenoid compounds have no benzene rings. Aromatic compounds can also have a heteroatom in the ring. This type of compound is known as a heterocyclic aromatic compound.



- (a) Aliphatic cyclic compound
- (b) Aromatic compound
- (c) Straight chain compound
- (d) Branched compound

**(B) Which of the following is a non-benzenoid aromatic compound?**

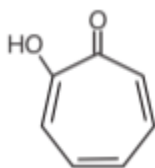
- (a) Anthracene
- (b) Cyclohexane
- (c) Naphthalene
- (d) Tropolone

**(C) Identify the pair of heterocyclic aromatic compounds.**

- (a) Benzene, Furan
- (b) Furan, Pyridine
- (c) Phenanthrene, Pyran
- (d) Cyclohexane, Benzene



**(D) The given structure can be classified as:**



- (a) Homocyclic aliphatic compound
- (b) Heterocyclic aromatic compound
- (c) Benzenoid aromatic compound
- (d) Non- benzenoid aromatic compound

**(E) What is the hybridisation of carbon in benzene?**

- (a)  $sp^2$
- (b)  $sp$
- (c)  $sp^3$
- (d) Not known

**Ans. (A)** (a) Aliphatic cyclic compound

**Explanation:** An alicyclic compound is a cyclic organic compound that is also aliphatic. They have one or more all-carbon rings that can be saturated or unsaturated but do not have aromatic properties. Alicyclic compounds may contain one or more aliphatic side chains.

**(B)** (d) Tropolone

**Explanation:** The primary distinction between benzenoid and non-benzenoid compounds is that benzenoid compounds have at least one benzene ring in the molecule, whereas compounds do not.

**(C)** (b) Furan, Pyridine non-benzenoid

**Explanation:** Examples of heterocyclic aromatic compounds are furan and pyridine. Due to the presence of non-localised lone pair. Furan is an aromatic compound with the oxygen lone pair participating in the  $\pi$ -electron system to satisfy Huckel's rule,  $4n+2$  ( $n = 1$ ) electrons. Pyridine is a cyclic, conjugated compound with three  $\pi$ -bonds. The molecule has six  $\pi$ -electrons, which is a Huckel number and it is aromatic.

**(D)** (d) Non-benzenoid aromatic compound

**Explanation:** Non-benzenoid compounds have no benzene rings in their structure but they follow the Huckel rule.

**(E)** (a)  $sp^2$



**Explanation:** The benzene hybridisation is said to be of the  $sp^2$  type. Benzene is made up of six carbon and six hydrogen atoms, with the central atom usually hybridised. The central atom in this case is carbon.

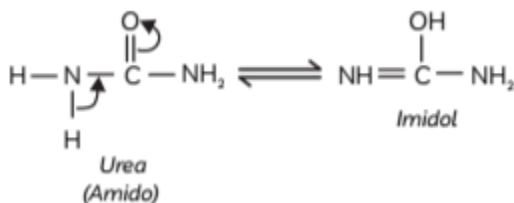
**2.** Organic chemistry has a nearly two-hundred- year history. Around the year 1780, chemists began to distinguish between organic molecules derived from plants and animals and inorganic compounds derived from mineral sources. Swedish chemist Berzelius believed that organic molecules were formed by a 'life force.' This theory was debunked in 1828 when F. Wohler synthesised urea from ammonium cyanate, an inorganic substance. Urea is a carbonyl group with two C-bound amine groups. The commercially available fertilizer has an analysis of 46-0-0 (N-P<sub>2</sub>O<sub>5</sub> - K<sub>2</sub>O). It has a role as a flour treatment agent, a human metabolite, a *Daphnia magna* metabolite, a *Saccharomyces cerevisiae* metabolite, an *Escherichia coli* metabolite, a mouse metabolite and a fertilizer. It is a monocarboxylic acid amide and a one-carbon compound. It derives from carbonic acid.

**(A)** Which was the first organic compound to be synthesised? Why does urea form tautomerism and not isomers?

**(B)** What is catenation?

**(C)** What is a benzenoid aromatic compound? Give the structure of naphthalene, phenanthrene and anthracene.

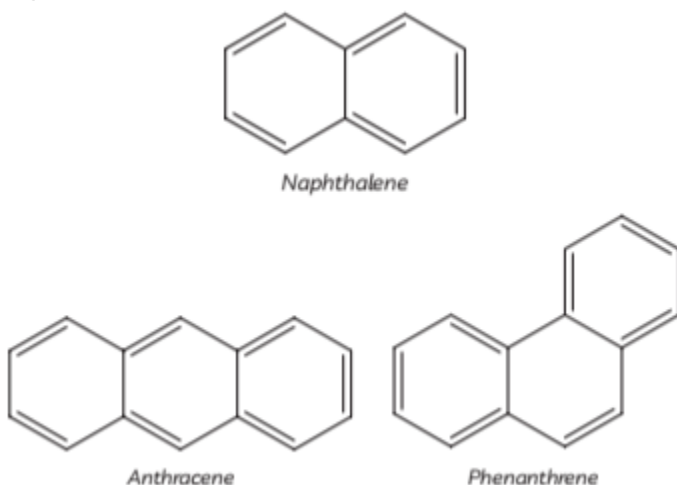
**Ans. (A)** F. Wohler created an organic chemical, urea, by converting an inorganic material, ammonium cyanate, into an organic compound. Urea ( $H_2N-CO-NH_2$ ) has only one structure. There is no isomerism in Urea. Urea has a "keto-imine" tautomeric structure that exists in equilibrium. But these are not isomers, rather they are tautomers.



**(B)** Catenation is the property by which an element binds to itself via covalent bonds to create chain or ring molecules. Carbon is the most typical element that undergoes catenation. It can form lengthy hydrocarbon chains and rings.

**(C)** Benzenoid aromatic compound is an aromatic compound with only benzene rings in its structure. Examples include naphthalene, aniline and others. A molecular structures

in which two carbon atoms are shared by two or more aromatic rings are fused aromatic rings.



**3.** Hyperconjugation is the interaction of electrons in a sigma ( $\sigma$ ) orbital (e.g., C-H or C-C) with an adjacent unoccupied non-bonding or antibonding  $\sigma^*$  or  $\pi^*$  orbital to give a pair of extended molecular orbitals. Hyperconjugation affects several properties like dipole moment, bond length, stability of carbocations, etc. The stability of carbocations is in the order:  $(\text{CH}_3)_3\text{C}^+ > (\text{CH}_3)_2\text{CH}^+ > (\text{CH}_3)\text{CH}_2^+ > \text{CH}_3^+$ . Inductive effect can be used to determine the stability of a molecule depending on the charge present on the atom and the groups bonded to the atom. The inductive effect also plays a vital role in deciding the acidity and basicity of a molecule. As the number of groups with increases, the acidic character increases; as the number groups with +1 effect increases the basic character increases. to

**(A)** What additional terminology is used describe hyperconjugation? In hyperconjugation, which bonding orbitals are involved in the overlapping?

**(B)** How many hyperconjugation structures -effect are possible for isopropyl radical?

**(C)** Answer the following questions:

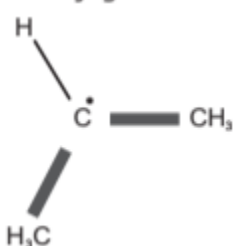
(i) Why ethene do not show hyperconjugation?

(ii) Arrange phenol, p-methyl phenol, m-nitrophenol and p-nitrophenol in order of increasing acidity.

**Ans. (A)** Hyperconjugation is also known as the Baker Nathan effect or no-bond resonance or  $\sigma - \pi$  conjugation. The Delocalisation of electrons or lone pair of  $\sigma$  - electrons into adjacent  $\pi$  - orbital or p-orbital is called hyperconjugation. It occurs due to overlapping of  $\sigma$  - bonding orbital or the orbital containing a lone pair with adjacent

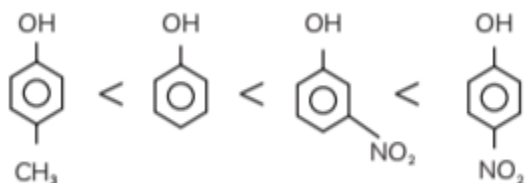
orbital  $\pi$  - or p-orbital.

**(B)** The number of hyperconjugative structures for isopropyl radical  $C_3H_7$  is 6. The unpaired electron is shared by a total of seven atoms in the isopropyl carbocation, one carbon atom and six hydrogen atoms, due to hyperconjugation.



**(C)** (i) Ethene does not show hyperconjugation as it is devoid of  $\alpha$  hydrogen. The presence of  $\alpha$ -hydrogen is the characteristic feature of hyperconjugation.

(ii) The order of increasing acidity is as follows:



**4.** The reaction mechanism (or reaction path) is the process, or pathway, by which a reaction occurs. Reaction mechanism involves the bond cleavage, attacking reagent, reaction intermediate and the electronic effects. Bond cleavage can be heterolytic or homolytic cleavage. The attacking reagents involve the electrophiles and nucleophiles. The next is the intermediate which includes carbocation (positively charged carbon), carbanion (negatively charged carbon) and free radicals (electrically neutral species). Last comes to the effects which include inductive effect, mesomeric effect, hyperconjugation and electrometric effect. Mesomeric or resonance effect is defined as the polarity produced in the molecule by the interaction of two  $\pi$ -bonds or between a  $\pi$ -bond and lone pair of electrons present on an adjacent atom. The resonance energy, or resonance stabilisation energy, is the difference in energy between the real inductive structure and the (most stable contributing structures) worst kinetic structure. The mesomeric effect is completely different from the inductive effect.

**(A) I, Cl, OH, CN and  $NH_3$  are referred as nucleophiles. Nucleophilic reagents behave. ....**

(a) salts

(b) Lewis's acid

- (c) Lewis bases
- (d) water

**(B) Which of the following is the correct statement regarding electrophile?**

- (a) Electrophiles are negatively charged species and can form a bond by accepting a pair of electrons from another electrophile.
- (b) Electrophiles are generally neutral species and can form a bond by accepting a pair of electrons from another nucleophile.
- (c) Electrophiles can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile.
- (d) Electrophiles are negatively charged species and can form a bond by accepting a pair of electrons from another electrophile.

**(C) Among the following which one is most reactive towards the electrophilic nitration?**

- (a) Benzene
- (b) Benzoic acid
- (c) Nitrobenzene
- (d) Toluene

**(D) Select the correct statement from the following option.**

- (a) Benzene ring has two different types of bond lengths for single and double bonds.
- (b) All the bond lengths in benzene are equal due to resonance.
- (c) All the bond length in benzene is equal due to hyperconjugation.
- (d) All of the above

**(E) How does increasing the number of alpha hydrogens affect hyper-conjugation?**

- (a) It will increase.
- (b) It will decrease.
- (c) It will remain the same.
- (d) Not defined.

**Ans. (A)** (c) Lewis bases

**Explanation:** Nucleophilic reagents are electron-rich species and thus they behave as Lewis bases. They attack on the electron-deficient area and in case of the same nucleophilic site, it parallels with the basicity. As the basicity increases the nucleophilicity also increases.



**(B)** (c) Electrophiles can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile.

**Explanation:** A chemical species that accepts an electron pair and forms bonds with nucleophiles is known as an electrophile. Electrophiles carry a positive charge and some are neutral in nature. They have a partial positive charge on an atom or lack an octet of electrons. They receive electrons therefore, they are Lewis acids. Some examples of electrophiles are

$\text{BF}_3$ ,  $\text{H}_3\text{O}^+$ ,  $\text{Cl}^+$ ,  $\text{F}^+$ , etc.

**(C)** (d) Toluene

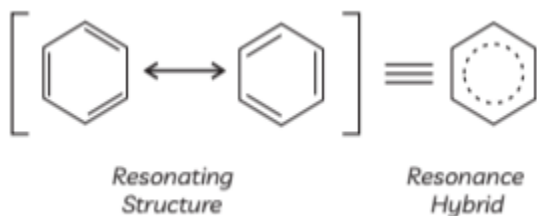
**Explanation:** In toluene, the  $-\text{CH}_3$  group is an electron-releasing group and the nitro group is an electron-withdrawing group. So, the electrophilic substitution of the  $-\text{NO}_2$  group is possible here. In benzene, also nitration is possible. But its reactivity toward electrophilic nitration is less than toluene due to the absence of electron releasing group. Benzoic acid has a  $-\text{COOH}$  group and it is an electron-withdrawing group. So, electrophilic nitration is less reactive. Similarly in nitrobenzene,  $-\text{NO}_2$  group is electron-withdrawing group. So, it is less reactive towards electrophilic nitration.



Structure of toluene

**(D)** (b) All the bond length in benzene is equal due to resonance.

**Explanation:** All the bond lengths in benzene are equal due to resonance.



**(E)** (a) It will increase

**Explanation:** On increasing the number of  $\alpha$ -H, the number of hyperconjugation structures increases. Hyperconjugation  $\propto$  number of  $\alpha$ -hydrogen.

Read the following passages and answer the questions that follow:

5. Essential oils are used in a wide variety of consumer goods such as detergents, soaps, toilet products, cosmetics, pharmaceuticals, perfumes, confectionery food products, soft



drinks, distilled alcoholic beverages (hard drinks) and insecticides. The world's production and consumption of essential oils and perfumes are increasing very fast. Production technology is an essential element to improve the overall yield and quality of essential oil. The traditional technologies pertaining to essential oil processing are of great significance and are still being used in many parts of the globe. Water distillation, water and steam distillation, steam distillation, cohobation, maceration and enfleurage are the most traditional and commonly used methods. Maceration is adaptable when oil yield from distillation is poor. Distillation methods are good for powdered almonds, rose petals and rose blossoms, whereas solvent extraction is suitable for expensive, delicate and thermally unstable materials like jasmine, tuberose and hyacinth. Water distillation is the most favoured method of production of citronella oil from plant material.

**(A) The method used for the extraction of oils from the flower is:**

- (a) Simple distillation
- (b) Steam distillation
- (c) Chromatography
- (d) Distillation under reduced pressure.

**(B) In steam distillation the substance starts to boil at:**

- (a)  $p = P_1 + P_2$
- (c)  $p = 2p_1 + P_2$
- (b)  $p = P_1 - P_2$
- (d)  $p = P_1 + 2P_2$

**(C) Choose the correct statement about the steam distillation.**

- (a) Separates the organic compounds have lesser solubility in an organic solvent.
- (b) Separates the mixtures of a compound having a small boiling point difference.
- (c) Separates the mixtures of the compound that have a higher solubility in one solvent and have a lower solubility in another solvent.
- (d) Separate substances that exist as steam which are volatile and these vapours are immiscible in water

**(D) In steam distillation, intramolecular hydrogen-bonded molecules are than intermolecular hydrogen-bonded molecules**

- (a) more flammable
- (b) non-flammable
- (c) less volatile





(d) more volatile

(E) Limonene can be isolated by which of the given methods?

(a) Fractional distillation

(b) Steam distillation

(c) Distillation under reduced pressure

(d) Simple distillation

**Ans. (A)** (b) Steam distillation

**Explanation:** The Steam distillation method can be used to separate oils from the flowers. These essential oils are immiscible in water and soluble at the vapour phase which is the principle of steam distillation. It is employed to remove aromatic compounds from a plant.

**(B)** (a)  $p = P_1 + P_2$

**Explanation:** In steam distillation, the boiling of liquid will start when the sum of the vapour pressure due to organic liquid

(P) and the sum of the vapour pressure due to water ( $P_1$ ) will be equal to the atmospheric pressure (p), i.e:  $p = P_1 + P_2$

**(C)** (d) Separate substances that exist as steam which are volatile and these vapours are immiscible in water

**Explanation:** It is used to separate substances that exist as steam which are volatile and these vapours are immiscible in water. In steam distillation, the liquid starts to boil when the sum of the vapour pressure due to organic liquid (p) & the sum of the vapour pressure due to water

( $p_2$ ) will be equal to the atmospheric pressure (p), i.e:  $p = P_1 + P_2$ . Since the vapour pressure of liquid is lower than the atmospheric pressure, the organic liquid vaporises at a low temperature below its boiling point.

**(D)** (d) More volatile.

**Explanation:** During boiling in the steam distillation, the strong intermolecular hydrogen bonding increases the boiling point but intramolecular hydrogen bonding does not increase the boiling point. So, the intramolecular hydrogen-bonded molecules are more volatile than intermolecular-bonded molecules.

(E) (b) Steam distillation

Explanation: Limonene is a high-boiling liquid which decomposes under the high

temperature, therefore steam distillation is used to obtain their oils, as distillation of co-mixture of oil and water at a lower boiling point.

**6.** The Carius halogen method in analytical chemistry is a method for the quantitative determination of halogens in chemical substances. A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as carius tube, in a furnace.

**(A)** What is the resulting salt formed at the end of the reaction?

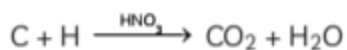
**(B)** The carbon and hydrogen will be converted to X and Y? What are the X and Y? What is the reaction that takes place during the reaction?

**(C)** What is the formula for estimating the percentage of the compound by the carius method?

**Ans. (A)** When silver nitrate reacts with halogen present in an organic compound a simple displacement reaction takes place which converts silver nitrate to insoluble precipitate of silver halide.

**(B)** The compounds X and Y are carbon dioxide and water. Which are obtained by the oxidation of carbon and hydrogen. So, the reaction that takes place here is oxidation. Nitric acid is used as an oxidising agent.

**(C)**



Percentage of halogen

$$= \frac{\text{Atomic mass of } X \times m_1 \times 100}{\text{Molecular mass of } AgX \times m}$$