

Exercises

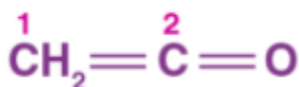
Question 12.1:

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

$\text{CH}_2=\text{C}=\text{O}$, $\text{CH}_3\text{CH}=\text{CH}_2$, $(\text{CH}_3)_2\text{CO}$, $\text{CH}_2=\text{CHCN}$, C_6H_6

Answer 12.1:

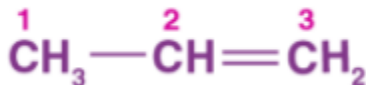
(i)



C-1 is sp^2 hybridised.

C-2 is sp hybridised.

(ii)

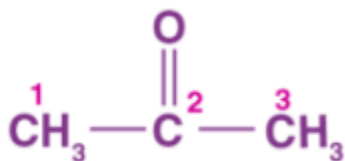


C-1 is sp^3 hybridised.

C-2 is sp^2 hybridised.

C-3 is sp^2 hybridised.

(iii)



C-1 and C-3 are sp^3 hybridised.

C-2 is sp^2 hybridised.

(iv)



C-1 is sp^2 hybridised.

C-2 is sp^2 hybridised.

C-3 is sp hybridised.

(v) C_6H_6

All the 6 carbon atoms in benzene are sp^2 hybridised.

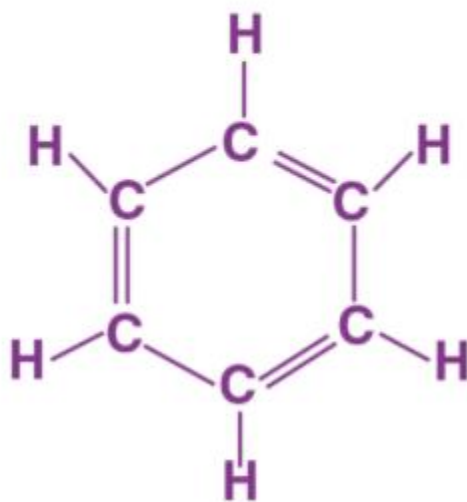
Question 12.2:

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 , $HCONHCH_3$

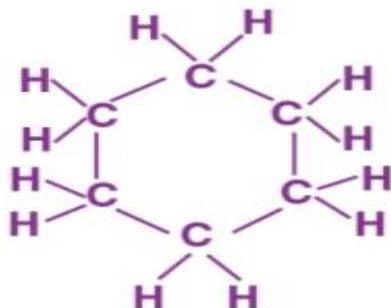
Answer 12.2:

(i) C_6H_6



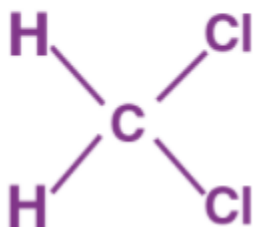
There are six C – C sigma bonds, six C–H sigma bonds, and three C=C pi resonating bonds in the given compound.

(ii) C_6H_{12}



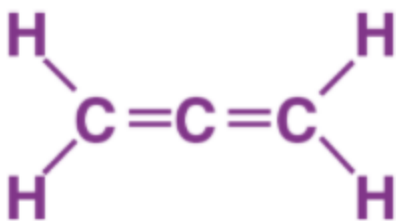
There are six C – C sigma bonds and twelve C–H sigma bonds in the given compound.

(iii) CH_2Cl_2



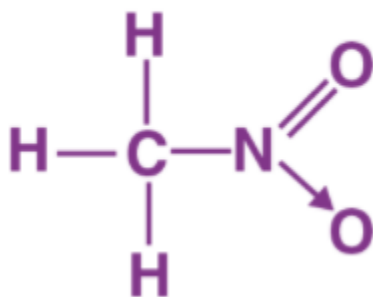
There are two C – Cl sigma bonds and two C–H sigma bonds in the given compound.

(iv) $\text{CH}_2 = \text{C} = \text{CH}_2$



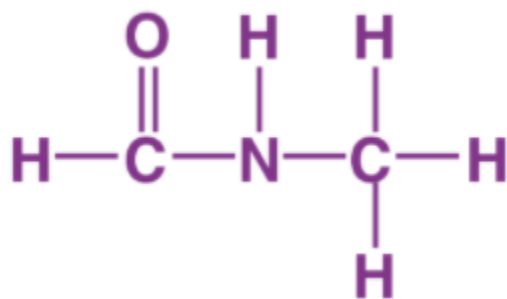
There are two C–C sigma bonds, four C–H sigma bonds, and two C=C pi bonds in the given compound.

(v) CH_3NO_2



There are three C–H sigma bonds, one C–N sigma bond, one N–O sigma bond, and one N=O pi bond in the given compound.

(vi) HCONHCH_3



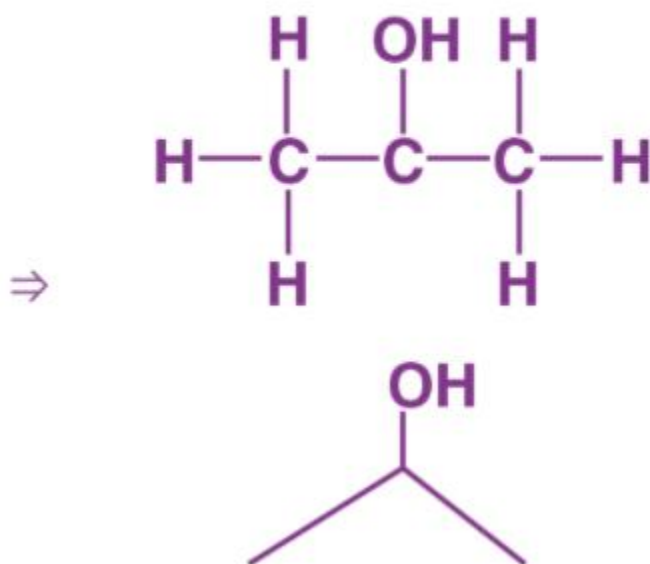
There are four C–H sigma bonds, two C–N sigma bond, one N–H sigma bond, and one C=O pi bond in the given compound.

Question 12.3:

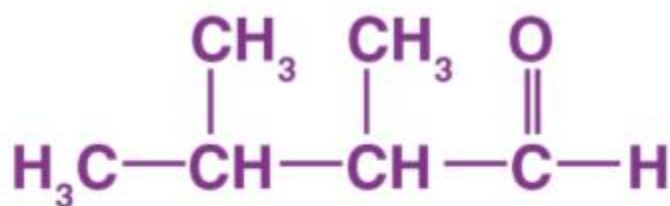
Write bond-line formulas for: Isopropyl alcohol, 2, 3–dimethyl butanal, Heptan–4–one.

Answer 12.3:

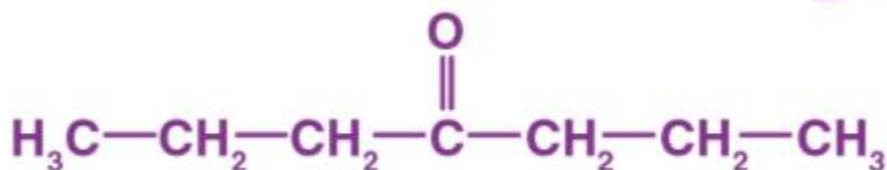
Isopropyl alcohol



2, 3–dimethyl butanal



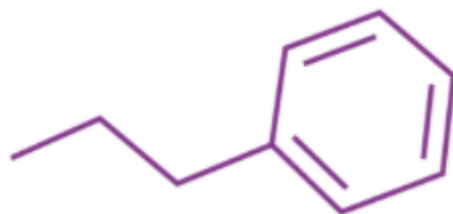
Heptan-4-one



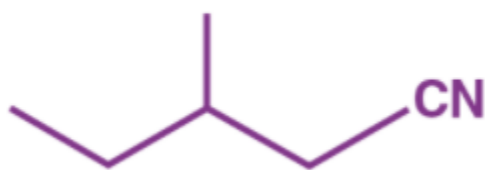
Question 12.4:

Give the IUPAC names of the following compounds:

(a)



(b)



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(c)



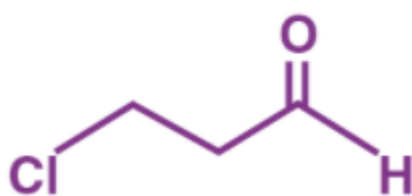
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(d)



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(e)

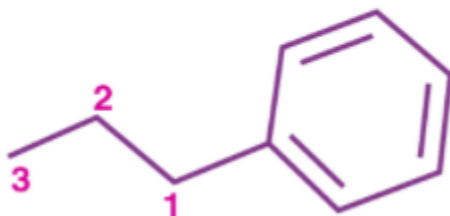


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(f) $\text{Cl}_2\text{CHCH}_2\text{OH}$

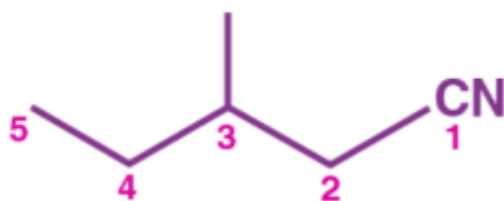
Answer 12.4:

(a)



Propylbenzene

(b)



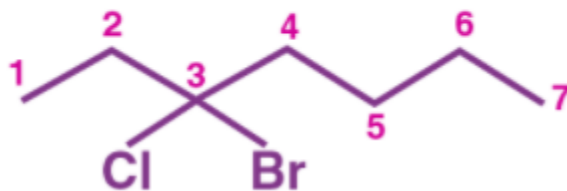
3-methylpentanenitrile

(c)



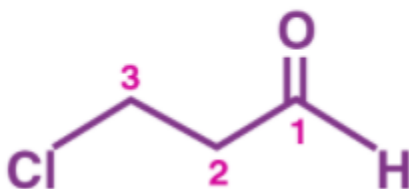
2, 5-dimethyl heptane

(d)



3-bromo-3-chloroheptane

(e)



3-chloropropanal

(f) $\text{Cl}_2\text{CHCH}_2\text{OH}$

2, 2-dichloroethanol

Question 12.5:

Which of the following represents the correct IUPAC name for 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

Answer 12.5:

(a) The prefix *di* shows that there are two methyl groups in the chain. Thus, the correct IUPAC name would be 2,2-Dimethylpentane.

(b) The locant number should start from the minimum. Here, 2,4,7 is lower than 2,5,7. Thus, the correct IUPAC name would be 2,4,7-Trimethyloctane.

(c) If the substituents in the chain are in equivalent positions, then the lower number is given to the substituent group in alphabetical order. Thus, the correct IUPAC name would be 2-Chloro-4-methylpentane.

(d) Out of the two functional groups present in the given compound, the alcoholic group is the principal functional group. Thus, the parent chain will have an -ol suffix. Since the alkyne group is in C-3, the IUPAC name would be But-3-yn-1-ol.

Question 12.6:

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

(a) $\text{H}-\text{COOH}$

(b) CH_3COCH_3

(c) $\text{H}-\text{CH}=\text{CH}_2$

Answer 12.6:

The first five members of each homologous series beginning with the given compounds are

(a)

$\text{H}-\text{COOH}$: Methanoic acid

CH_3-COOH : Ethanoic acid

$\text{CH}_3-\text{CH}_2-\text{COOH}$: Propanoic acid

$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{COOH}$: Butanoic acid

$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$: Pentanoic acid

(b)

CH_3COCH_3 : Propanone

$\text{CH}_3\text{COCH}_2\text{CH}_3$: Butanone

$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$: Pentan-2-one

$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$: Hexan-2-one

$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$: Heptan-2-one

(c)

$\text{H}-\text{CH}=\text{CH}_2$: Ethene

$\text{CH}_3-\text{CH}=\text{CH}_2$: Propene

$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$: 1-Butene

$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$: 1-Pentene

$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$: 1-Hexene

Question 12.7:

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

Answer 12.7:

(a) 2, 2, 4-trimethylpentane

Condensed formula



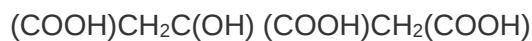
Bond line formula:



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(b) 2-hydroxy-1, 2, 3-propanetricarboxylic acid

Condensed Formula



Bond line formula:



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Functional groups:

Carboxylic acid(-COOH) and Hydroxyl (-OH) groups

(c) Hexanedial

Condensed Formula



Bond line formula:



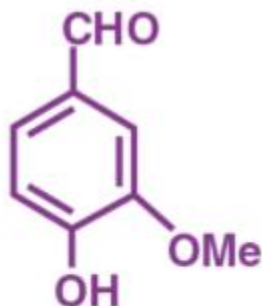
Functional groups:

Aldehyde(-CHO)

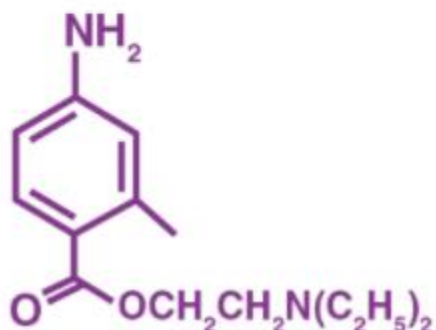
Question 12.8:

Identify the functional groups in the following compounds.

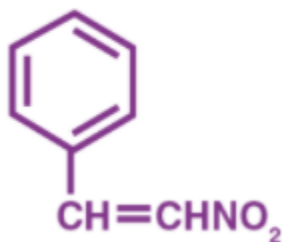
(a)



(b)

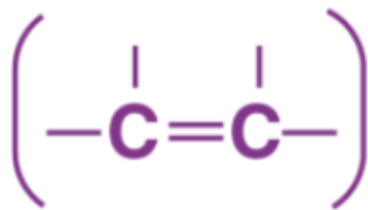


(c)



Answer 12.8:

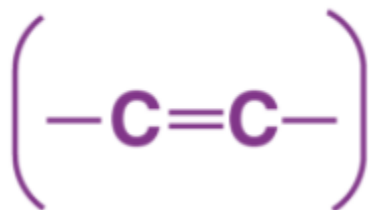
(a) Hydroxyl ($-\text{OH}$), Aldehyde ($-\text{CHO}$), Methoxy ($-\text{OMe}$),
C=C double bond



(b) Ester ($-\text{O}=\text{C}-\text{O}-$), 1° Amino ($-\text{NH}_2$) (aromatic), Diethylamine ($\text{N}(\text{C}_2\text{H}_5)_2$) – 3° Amino

(c) Nitro ($-\text{NO}_2$),

C=C Ethylenic double bond



Question 12.9:

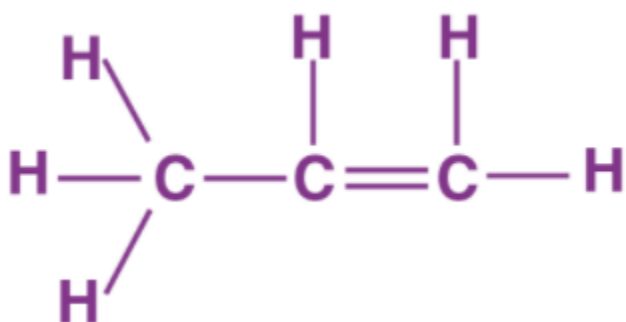
Which of the two: $\text{O}_2\text{NCH}_2\text{CH}_2\text{O}^-$ or $\text{CH}_3\text{CH}_2\text{O}^-$ is expected to be more stable and why?

Answer 12.9:

Since NO_2 belongs to the electron-withdrawing group, it shows $-I$ effect. NO_2 tries to decrease the negative charge on the compound by withdrawing the electrons toward it. This stabilizes the compound whereas the ethyl group belongs to the electron-releasing group and shows $+I$ effect. This results in an increase in the negative charge on the compound thus destabilizing the compound. Hence, I would expect $\text{O}_2\text{NCH}_2\text{CH}_2\text{O}^-$ to be more stable than $\text{CH}_3\text{CH}_2\text{O}^-$.

Question 12.10:

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

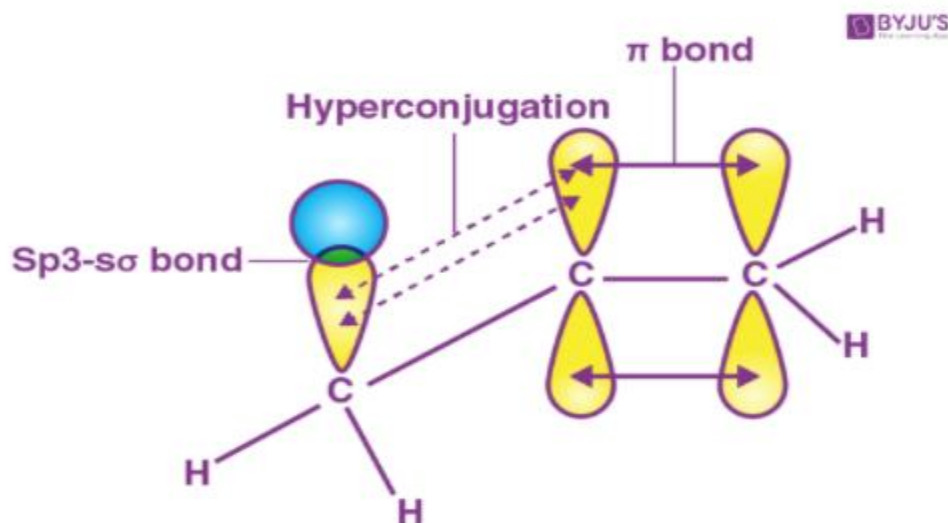


Answer 12.10:

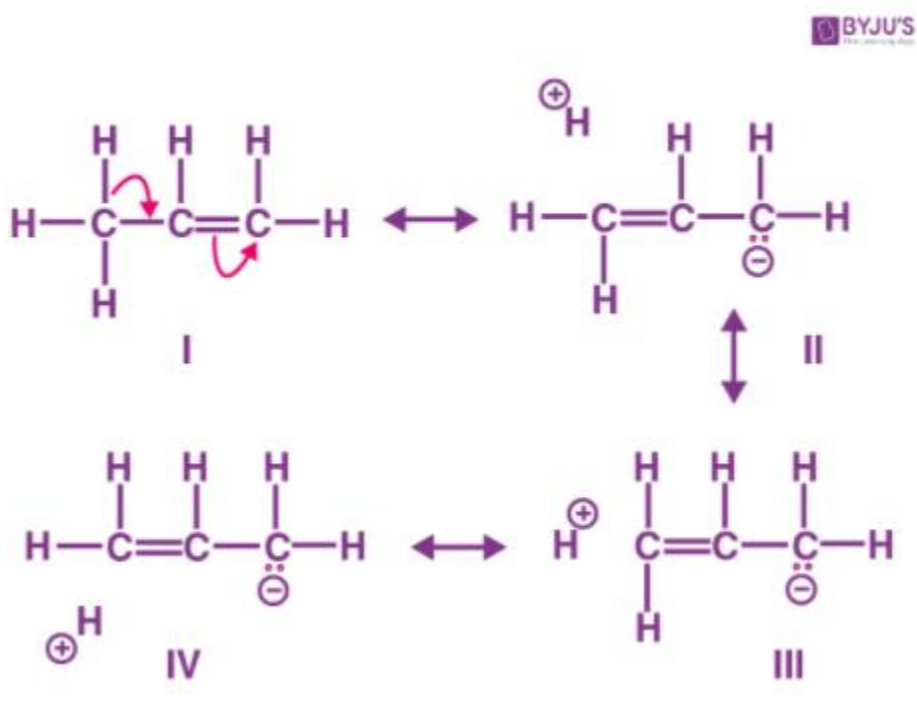
Due to hyperconjugation, an alkyl group behaves as an electron-donor group when attached to a π system. For example, look at propene.

The sigma electrons of the C-H bond get delocalized due to hyperconjugation. The alkyl is attached directly to an unsaturated system. The delocalization happens due to the partial overlap of an $\text{sp}^3\text{-s}$ sigma bond orbital with an empty p orbital of the π bond of an adjacent carbon atom.

This process can be shown as:



The overlap as shown above results in delocalization making the compounds more stable.



Question 12.11:

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

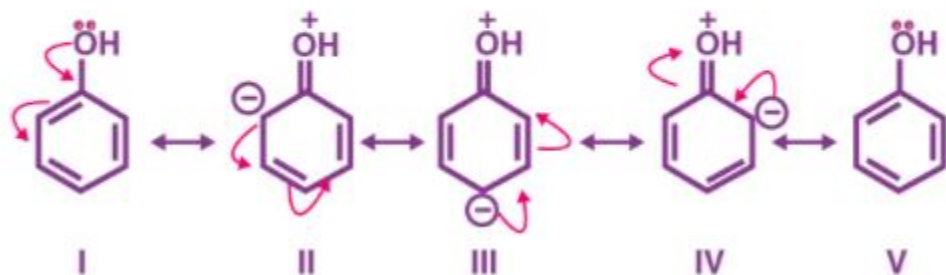
- (a) $\text{C}_6\text{H}_5\text{OH}$
- (b) $\text{C}_6\text{H}_5\text{NO}_2$
- (c) $\text{CH}_3\text{CH}=\text{CH}-\text{CHO}$
- (d) $\text{C}_6\text{H}_5\text{CHO}$
- (e) $\text{C}_6\text{H}_5-\text{CH}_2$
- (f) $\text{CH}_3\text{CH}=\text{CHCH}_2$

Answer 12.11:

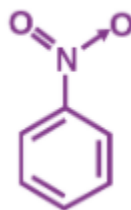
(a) The structure of $\text{C}_6\text{H}_5\text{OH}$ is:



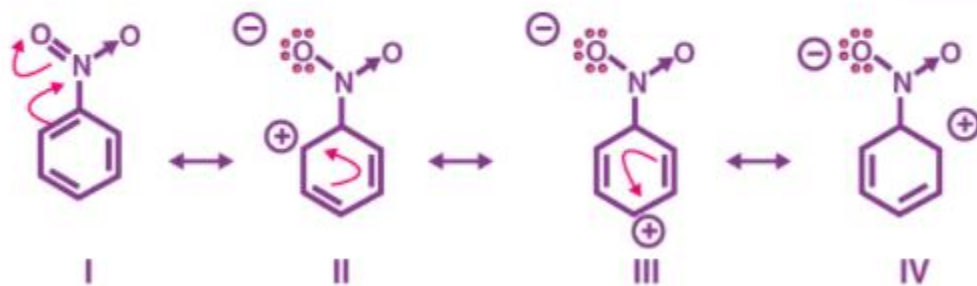
Resonating structures:



(b) The structure of $C_6H_5NO_2$ is:

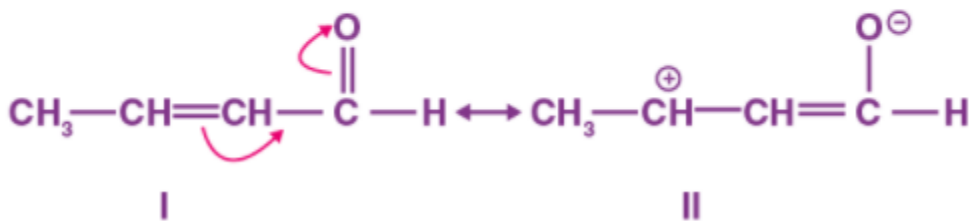


Resonating structures:

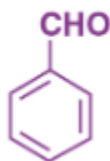


(c) $CH_3CH=CH-CHO$

Resonating structures:



(d) The structure of C_6H_5CHO is:

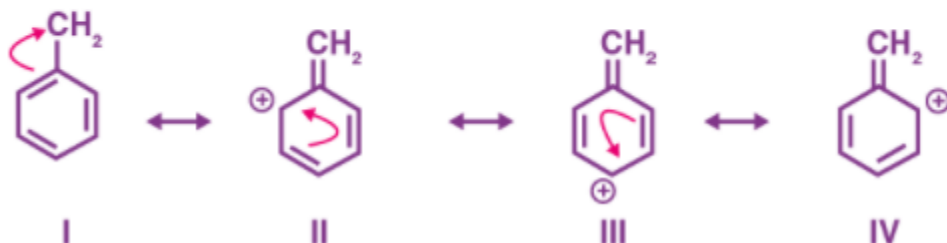


Resonating structures:



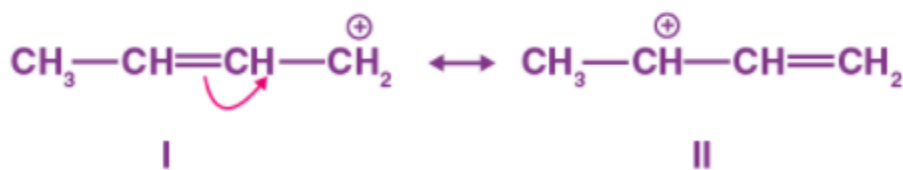
(e) $C_6H_5-CH_2$

Resonating structures:



(f) $CH_3CH=CHCH_2^+$

Resonating structures:



Question 12.12:

What are electrophiles and nucleophiles? Explain with examples.

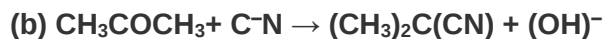
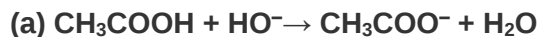
Answer 12.12:

A nucleophile is a reagent that has an electron pair and is willing to donate it. It is also known as a nucleus-loving reagent. Ex: NC^- , OH^- , R_3C^- (carbanions), etc.

An electrophile is a reagent which is in need of an electron pair and is also known as an electron-loving pair. Ex: Carbonyl groups, CH_3CH_2^+ (Carbocations), Neutral molecules (due to the presence of a lone pair).

Question 12.13:

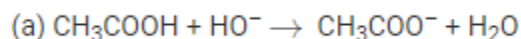
Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles:



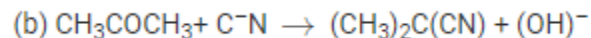
Answer 12.13:

A nucleophile is a reagent that has an electron pair and is willing to donate it. It is also known as a nucleus-loving reagent.

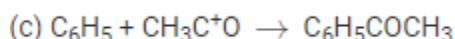
An electrophile is a reagent which is in need of an electron pair and is also known as an electron-loving pair.



It is a nucleophile since HO^- is electron rich in nature.



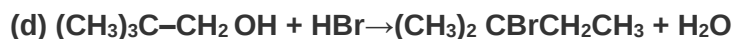
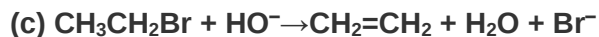
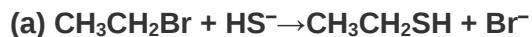
It is a nucleophile since C^-N is electron rich in nature.



It is an electrophile since $\text{CH}_3\text{C}^+\text{O}$ is electron-deficient in nature.

Question 12.14:

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

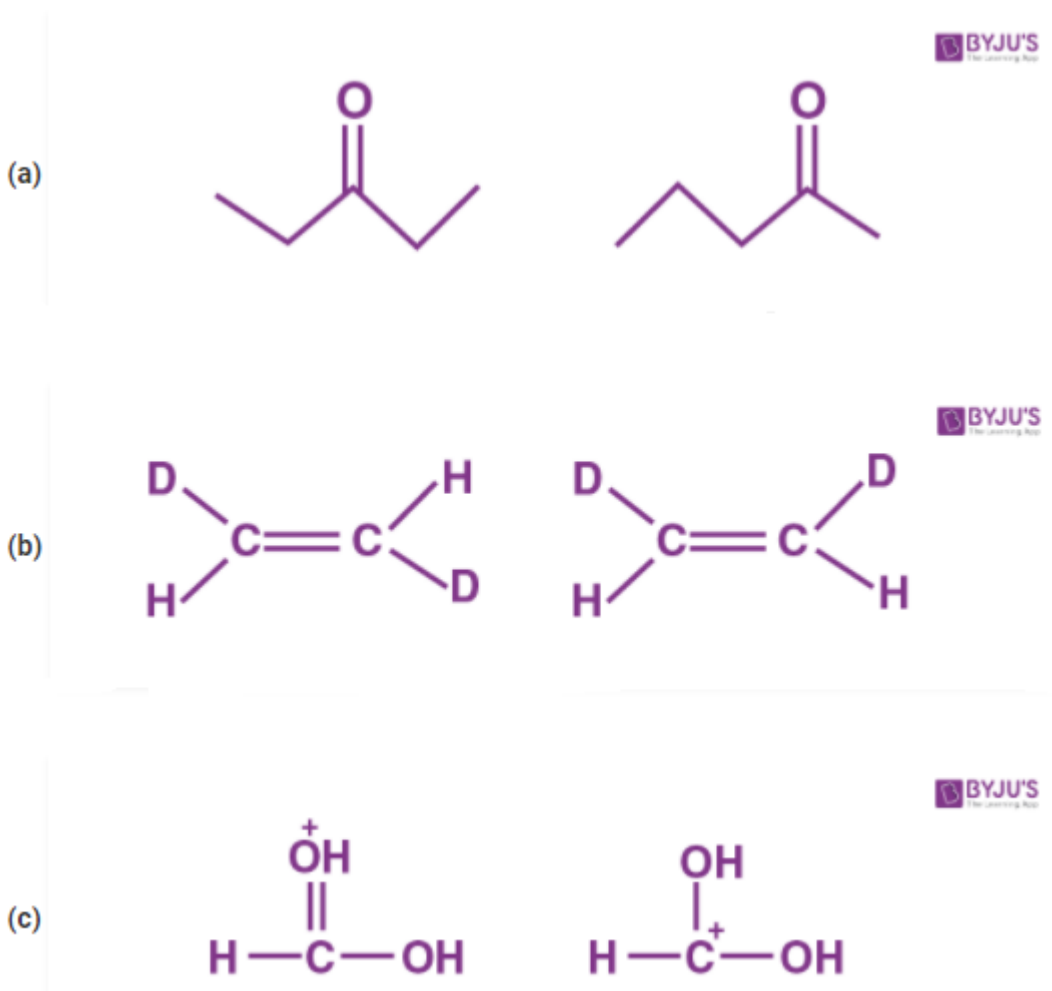


Answer 12.14:

- (a) Substitution (nucleophilic) reaction since bromine group gets substituted by $-\text{SH}$ group.
- (b) Addition (electrophilic) reaction since two reactant molecules combine to form a single product.
- (c) Elimination (bimolecular) reaction since reaction hydrogen and bromine are removed to form ethene.
- (d) Substitution (nucleophilic) reaction since rearrangement of atoms takes place.

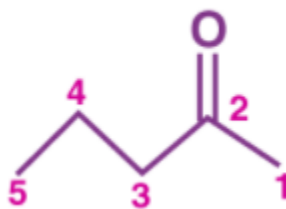
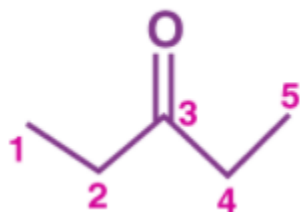
Question 12.15:

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

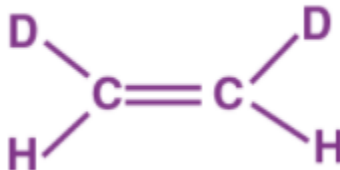
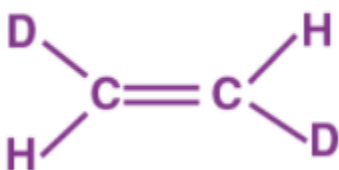


Answer 12.15:

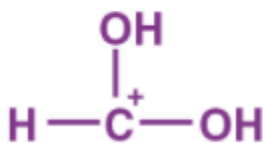
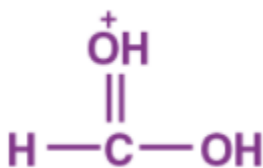
- (a) The given compounds are a pair of structural isomers since they have the same molecular formula but have different structures. These compounds differ in the position of the ketone group. For the first structure, it is in C-3 whereas, for the 2nd one, it is in C-2.



(b) The given compounds are a pair of geometrical isomers since they have the same molecular formula, sequence of covalent bonds and the same constitution but differ in the relative positioning of the atoms in space. These compounds differ in the positioning of the Deuterium and Hydrogen.



(c) The given compounds are a pair of contributing structures or canonical structures. They do not represent any real molecule and are purely hypothetical. They are also called resonance isomers.



Question 12.16:

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)



(b)



(c)

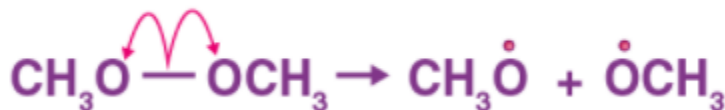


(d)



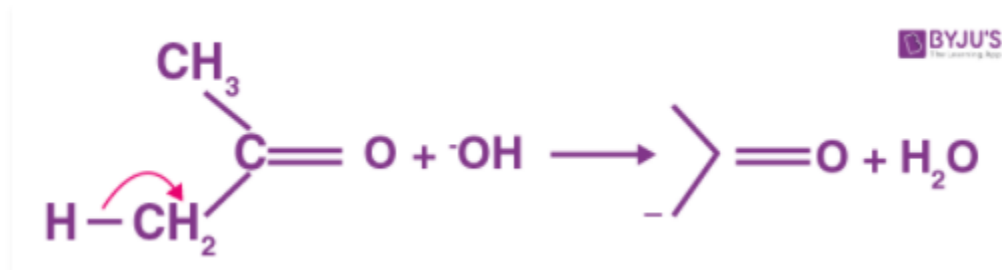
Answer 12.16:

(a) The bond cleavage can be shown as:



It comes under homolytic cleavage since one of the shared pair in a covalent bond goes with the bonded atom. A free radical is formed as the reaction intermediate.

(b) The bond cleavage can be shown as:



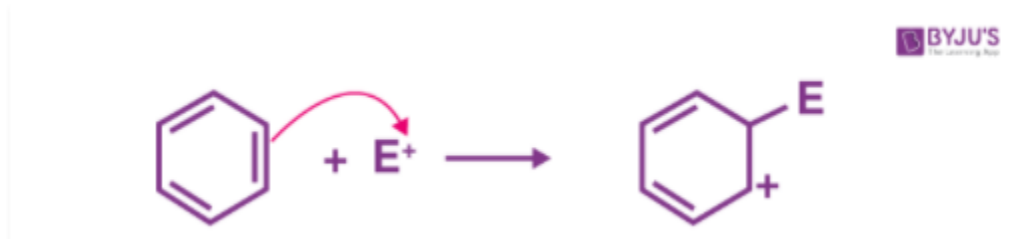
It comes under heterolytic cleavage since the shared remains with the carbon atom of propanone. A carbanion is formed as the reaction intermediate.

(c) The bond cleavage can be shown as:



It comes under heterolytic cleavage since the shared remains with the bromine ion. A carbocation is formed as the reaction intermediate.

(d) The bond cleavage can be shown as:



It comes under heterolytic cleavage since the shared remains with one of the fragments. A carbocation is formed as the reaction intermediate.

Question 12.17:

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

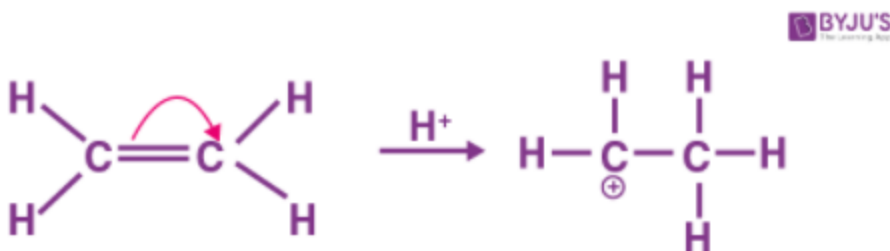
(a) $\text{Cl}_3\text{CCOOH} > \text{Cl}_2\text{CHCOOH} > \text{ClCH}_2\text{COOH}$

(b) $\text{CH}_3\text{CH}_2\text{COOH} > (\text{CH}_3)_2\text{CHCOOH} > (\text{CH}_3)_3\text{C.COOH}$

Answer 12.17:

Electrometric effect

The complete transfer of the shared pair of π electrons to either of the two atoms linked by multiple bonds in the presence of an attacking agent is called the electrometric effect. It can either be $-E$ effect or $+E$ effect.



$-E$ effect: Occurs when electrons are moved away from the attacking agent

$+E$ effect: Occurs when electrons are moved towards the attacking agent

Inductive effect

Inductive effect involves the permanent displacement of sigma (σ) electrons along a saturated chain, whenever an electron withdrawing or electron donating group is present.

It can either be $+I$ effect or $-I$ effect. When an atom or group attracts electrons towards itself more strongly than hydrogen, it is said to possess $-I$ effect.



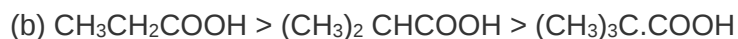
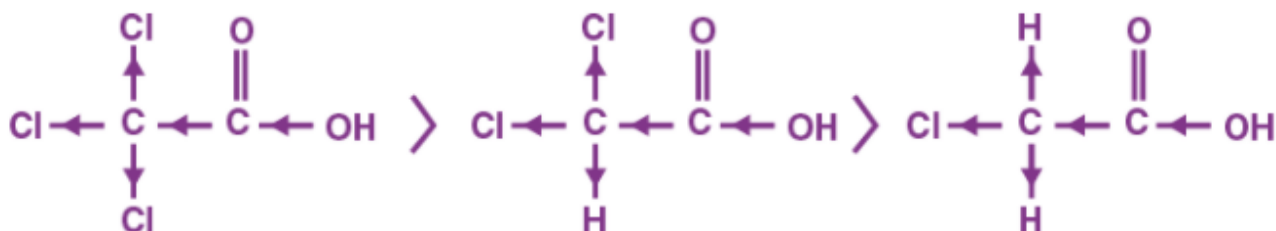
When the force with which an atom attracts electrons towards itself is greater than that of hydrogen, it is said to exhibit $+I$ effect.



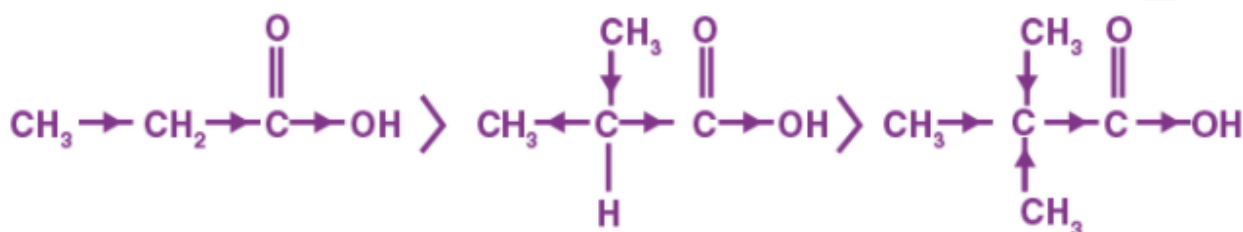
When the force with which an atom attracts electrons towards itself is greater than that of hydrogen, it is said to exhibit $+I$ effect.



The acidity increases with the increase in $-I$ effect which is directly proportional to the number of chlorine atoms.



The acidity increases with the increase in $+I$ effect which is directly proportional to the number of alkyl groups.



Question 12.18:

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

(a) Crystallisation

(b) Distillation

(c) Chromatography

Answer 12.18:

(a) Crystallisation

Crystallization is used to purify solid organic compounds.

Principle: The principle on which it works is the difference in the solubility of the compound and impurities in a given solvent. The impure compound is made to dissolve in the solvent at a higher temperature since it is sparingly soluble at lower temperatures. This is continued till we get an almost saturated solution. On cooling and filtering it, we get its' crystals. Ex: By crystallizing 2-4g of crude aspirin in 20mL of ethyl alcohol, we get pure aspirin. It is heated if needed and left undisturbed until it crystallizes. The crystals are then separated and dried.

(b) Distillation

This method is used to separate non-volatile liquids from volatile impurities. It is also used when the components have a considerable difference in their boiling points.

Principle: The principle on which it works is that liquids having different boiling points vaporise at different temperatures. They are then cooled and the formed liquids are separated.

Ex: A mixture of aniline (b.p = 457 K) and chloroform (b.p = 334 K) is taken in a round bottom flask having a condenser. When they are heated, Chloroform, vaporizes first due to its high volatility and made to pass through a condenser where it cools down. The aniline is left behind in the round bottom flask.

(c) Chromatography

It is widely used for the separation and purification of organic compounds.

Principle: The principle on which it works is that individual components of a mixture move at different paces through the stationary phase under the influence of mobile phase.

Ex: **Chromatography** can be used to separate a mixture of blue and red ink. This mixture is placed on chromatogram where the component which is less absorbed by the chromatogram moves faster up the paper than the other component which is almost stationary.