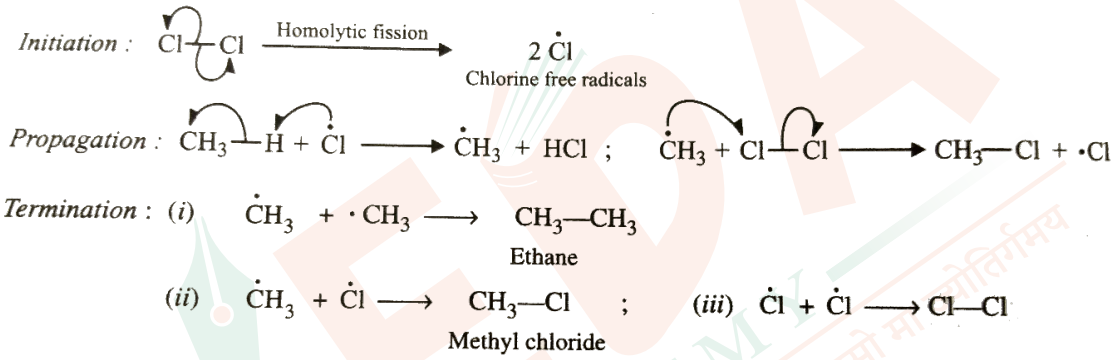
Q. 1. **How do you account for the formation of ethane during chlorination of methane?**

ANSWER:-

Chlorination of methane is a free radical reaction which occurs by the following mechanism:



From the given mechanism, it is evident that during the propagation step, $\cdot CH_3$ (methyl) free radicals are generated, which can undergo three possible reactions (i)-(iii). In the chain termination step, two $\cdot CH_3$ radicals combine to form ethane (C_2H_6), concluding the radical chain reaction.

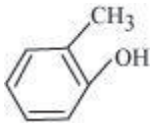
Q. 2. **Write IUPAC names of the following compounds:**

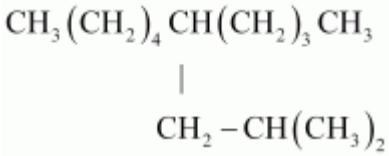
(a) $CH_3CH = C(CH_3)$

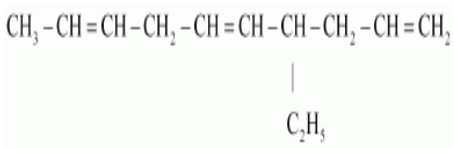
(b) $CH_2 = CH - C \equiv C - CH_3$

(d) 

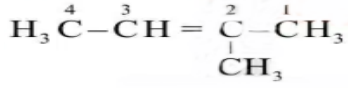
(c) 

(e) 

(f) 

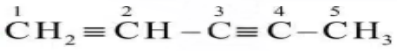
(g) 

ANSWER:-

(a) 

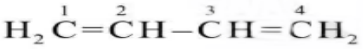
IUPAC name: 2-Methylbut-2-ene

(b)



IUPAC name: Pen-1-ene-3-yne

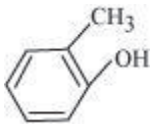
(c)  can be written as:



IUPAC name: 1, 3-Butadiene or Buta-1, 3-diene

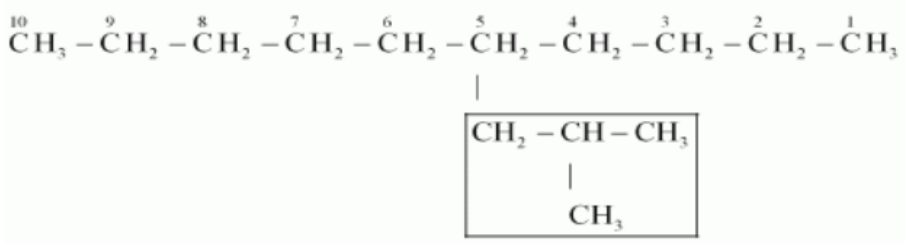
(d)  $-CH_2-CH_2-CH=CH_2$

IUPAC name: 4-Phenyl but-1-ene

(e) 

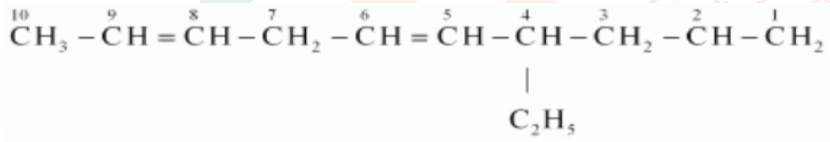
IUPAC name: 2-methylphenol

(f)



IUPAC name: 5-(2-Methylpropyl)-decane

(f)



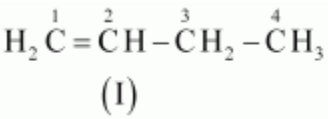
IUPAC name: 4-Ethyldeca-1, 5, 8-triene

Q. 3. **For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bond as indicated:**

(a) C_4H_8 (one double bond) **(b) C_5H_8 (one triple bond)**

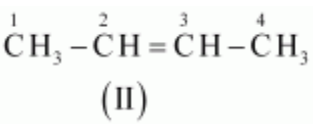
ANSWER:-

(a) The following structural isomers are possible for C_4H_8 with one double bond:



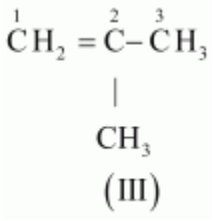
(I)

But-1-ene



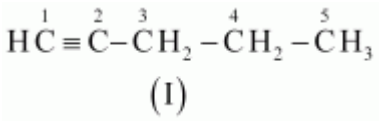
(II)

But-2-ene

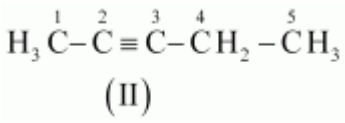


2-Methylprop-1-ene.

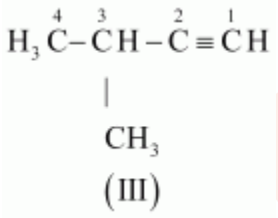
(b) The following structural isomers are possible for C_5C_8 with one triple bond:



Pent-1-yne



Pent-2-yne



3-Methylbut-1-yne.

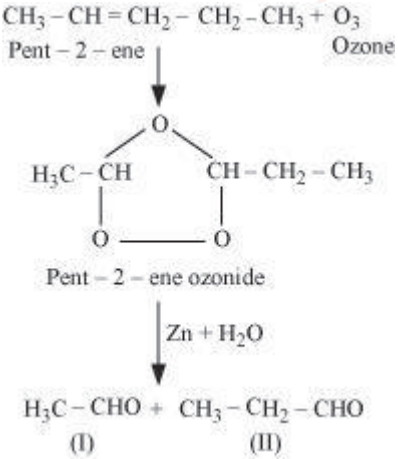
Q. 4. Write IUPAC names of the products obtained by the ozonolysis of the following compounds:

(i) Pent-2-ene **(ii) 3, 4-Dimethylhept-3-ene**

(iii) 2-Ethylbut-1-ene **(iv) 1-Phenylbut-1-ene**

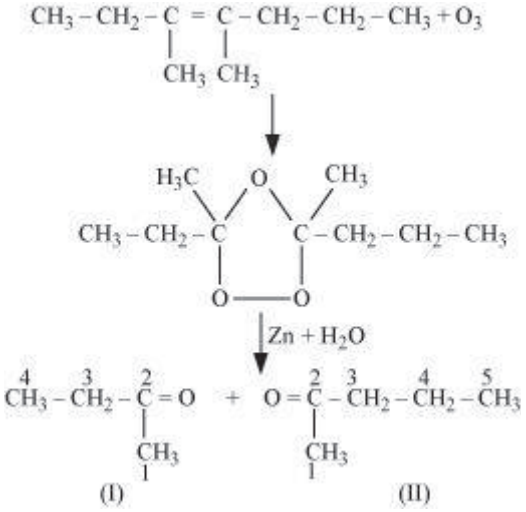
ANSWER:-

(i) Pent-2-ene undergoes ozonolysis as:



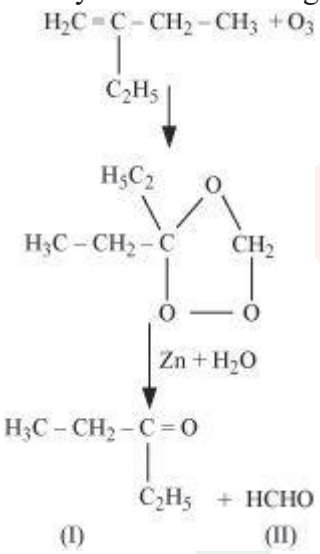
The IUPAC name of Product (I) is ethanal and Product (II)is propanal.

(ii) 3, 4-Dimethylhept-3-ene undergoes ozonolysis as:



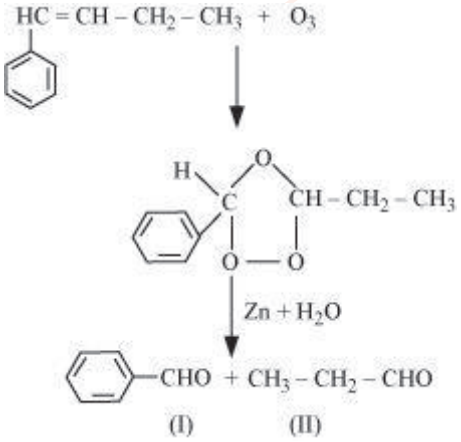
The IUPAC name of Product (I)is butan-2-one and Product (II)is Pentan-2-one.

(iii) 2-Ethylbut-1-ene undergoes ozonolysis as:



The IUPAC name of Product (I)is pentan-3-one and Product (II)is methanal.

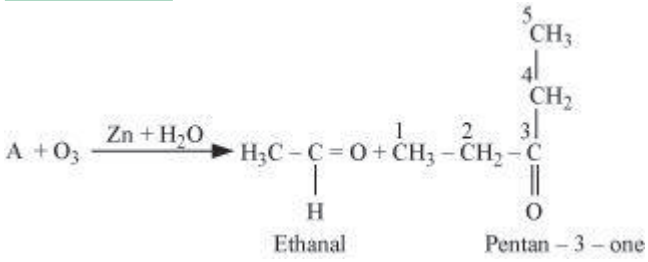
(iv) 1-Phenylbut-1-ene undergoes ozonolysis as:



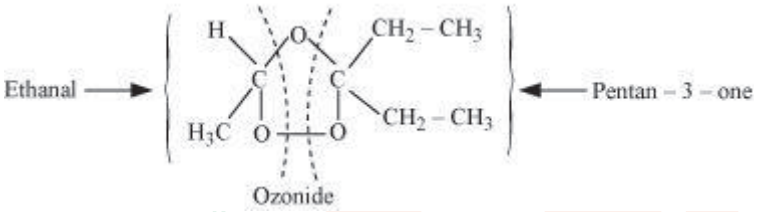
The IUPAC name of Product (I)is benzaldehyde and Product (II)is propanal.

Q. 5. **An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of 'A'.**

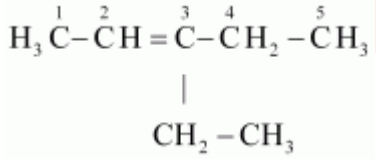
ANSWER:-



During ozonolysis, a cyclic ozonide intermediate is formed, which subsequently undergoes cleavage to yield the final products. Given that ethanal and pentan-3-one are obtained from the intermediate ozonide, the expected structure of the ozonide corresponds to the alkene that would lead to these cleavage products.



This ozonide is formed as an addition of ozone to 'A'. The desired structure of 'A' can be obtained by the removal of ozone from the ozonide. Hence, the structural formula of 'A' is:



The IUPAC name of 'A' is 3-Ethylpent-2-ene.

Q. 6. **An alkene 'A' contains three C – C, eight C – H σ bonds and one C – C π bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write IUPAC name of 'A'.**

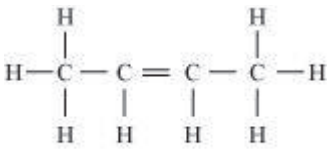
ANSWER:-

As per the given information, 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. The formation of two moles of an aldehyde indicates the presence of identical structural units on both sides of the double bond containing carbon atoms. Hence, the structure of 'A' can be represented as:

XC = CX

There are eight C–H σ bonds. Hence, there are 8 hydrogen atoms in 'A'. Also, there are three C–C bonds. Hence, there are four carbon atoms present in the structure of 'A'.

Combining the inferences, the structure of 'A' can be represented as:

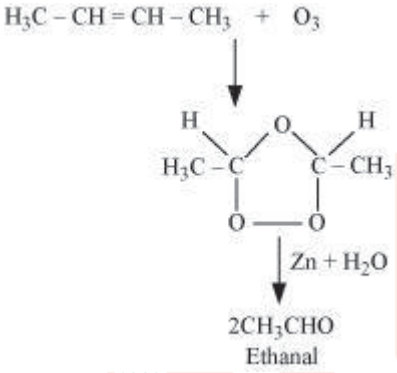


(A)

A' has 3 C–C bonds, 8 C–H σ bonds, and one C–C π bond.

Hence, the IUPAC name of 'A' is But-2-ene.

Ozonolysis of 'A' takes place as:



The final product is ethanal with molecular mass

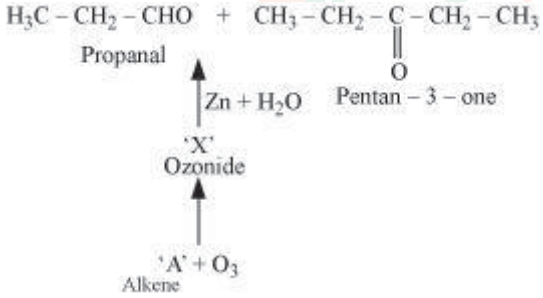
$=\left[(2\times12)+(4\times1)+(1\times16)\right]$

$=44$ u

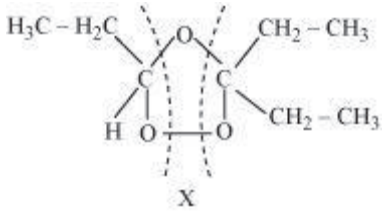
Q. 7. Propanal and pentan-3-one are the ozonolysis products of an alkene? What is the structural formula of the alkene?

ANSWER:-

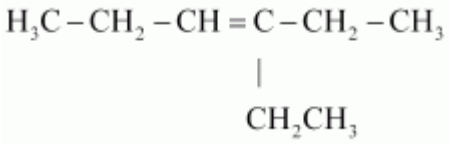
As per the given information, propanal and pentan-3-one are the ozonolysis products of an alkene. Let the given alkene be 'A'. Writing the reverse of the ozonolysis reaction, we get:



The products are obtained on the cleavage of ozonide 'X'. Hence, 'X' contains both products in the cyclic form. The possible structure of ozonide can be represented as:



Now, 'X' is an addition product of alkene 'A' with ozone. Therefore, the possible structure of alkene 'A' is:



Q. 8. Write chemical equations for combustion reaction of the following hydrocarbons:

(i) Butane (ii) Pentene (iii) Hexyne (iv) Toluene

ANSWER:-

Combustion is a chemical reaction in which a substance reacts rapidly with oxygen to produce heat. It is typically an exothermic oxidation reaction, commonly occurring with hydrocarbons, resulting in the formation of carbon dioxide (CO_2) and water (H_2O) when complete.

(i) $2C_4H_{10(g)} + 13O_{2(g)} \longrightarrow 8CO_{2(g)} + 10H_2O_{(g)} + \text{Heat}$

Butane

(ii) $2C_5H_{10(g)} + 15O_{2(g)} \longrightarrow 10CO_{2(g)} + 10H_2O_{(g)} + \text{Heat}$

Pentene

(iii) $2C_6H_{10(g)} + 17O_{2(g)} \longrightarrow 12CO_{2(g)} + 10H_2O_{(g)} + \text{Heat}$

Hexyne

(iv) 

Toluene

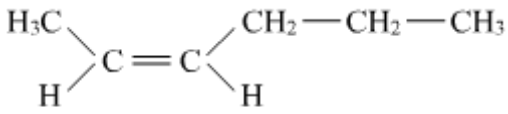
Q. 9. Draw the cis and trans structures of hex-2-ene. Which isomer will have higher b.p. and why?

ANSWER:-

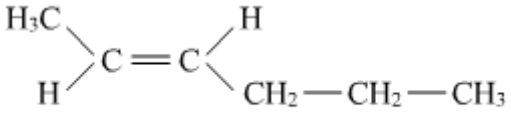
Hex-2-ene is represented as:

$CH_3 — CH = CH — CH_2 — CH_2 — CH_3$

Geometrical isomers of hex-2-ene are:



cis-isomer



trans-isomer

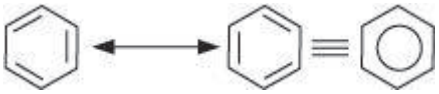
In the cis-isomer, the dipole moments of the C–CH_3 and C–$CH_2CH_2CH_3$ bonds align in the same direction, resulting in a higher overall dipole moment. In contrast, in the trans-isomer, these dipole moments act in opposite directions, partially cancelling each other out, leading to a lower net dipole moment.

Since the cis-isomer is more polar, it experiences stronger intermolecular dipole-dipole interactions, which contribute to a higher boiling point compared to the trans-isomer.

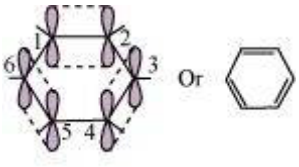
Q. 10. Why is benzene extra ordinarily stable though it contains three double bonds?

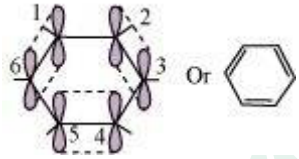
ANSWER:-

Benzene is a hybrid of resonating structures given as:



All six carbon atoms in benzene are sp^2 hybridized. The two sp^2 hybrid orbitals of each carbon atom overlap with the sp^2 hybrid orbitals of adjacent carbon atoms to form six sigma bonds in the hexagonal plane. The remaining sp^2 hybrid orbital on each carbon atom overlaps with the s-orbital of hydrogen to form six sigma C–H bonds. The remaining unhybridized p-orbital of carbon atoms has the possibility of forming three π bonds by the lateral overlap of $C_1 - C_2$, $C_3 - C_4$, $C_5 - C_6$, or $C_2 - C_3$, $C_4 - C_5$, $C_6 - C_1$.





The six π's are delocalized and can move freely about the six carbon nuclei. Even after the presence of three double bonds, these delocalized π-electrons stabilize benzene.

Q. 11. What are the necessary conditions for any system to be aromatic?

ANSWER:-

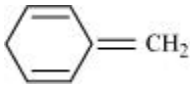
A compound is said to be aromatic if it satisfies the following three conditions:

(i) It should have a planar structure.

(ii) The π–electrons of the compound are completely delocalized in the ring.

(iii)The total number of π–electrons present in the ring should be equal to (4n + 2), where n = 0, 1, 2 … etc. This is known as Huckel's rule.

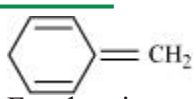
Q. 12. Explain why the following systems are not aromatic?

(i) 

(ii) 

(iii) 

ANSWER:-

(i) 

For the given compound, the number of π-electrons is six. But only four π-electrons are present within the ring. Also there is no conjugation of π-electrons within the ring and the compound is not planar in shape. Hence, the given compound is not aromatic in nature.

(ii) 

For the given compound, the number of π-electrons is four.

By Huckel's rule,

$4n + 2 = 4$

$4n = 2$

$n = \frac{1}{2}$

For a compound to be aromatic, the value of n must be an integer (n = 0, 1, 2…), which is not true for the given compound. Hence, it is not aromatic in nature.

(iii) 

For the given compound, the number of π-electrons is eight.

By Huckel's rule,

$4n + 2 = 8$

$4n = 6$

$n = \frac{3}{2}$

For a compound to be aromatic, the value of n must be an integer (n = 0, 1, 2…). Since the value of n is not an integer, the given compound is not aromatic in nature.

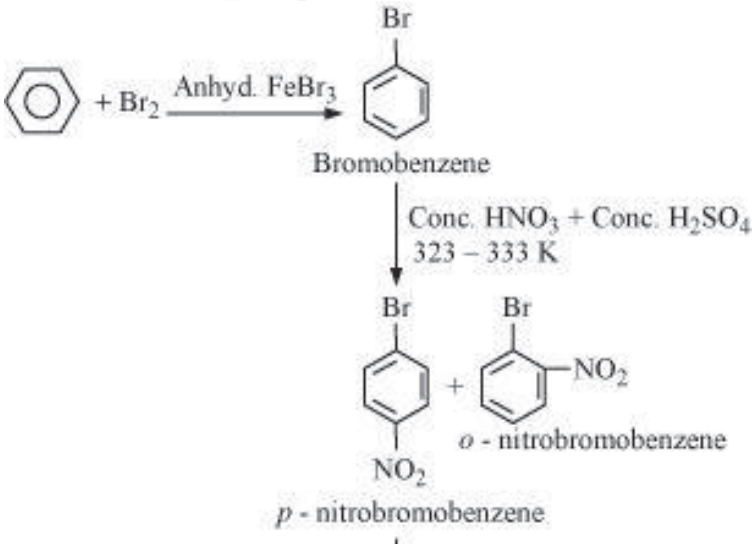
Q. 13. How will you convert benzene into

(i) p-nitrobromobenzene **(ii) m-nitrochlorobenzene**

(iii) p -nitrotoluene **(iv) acetophenone**

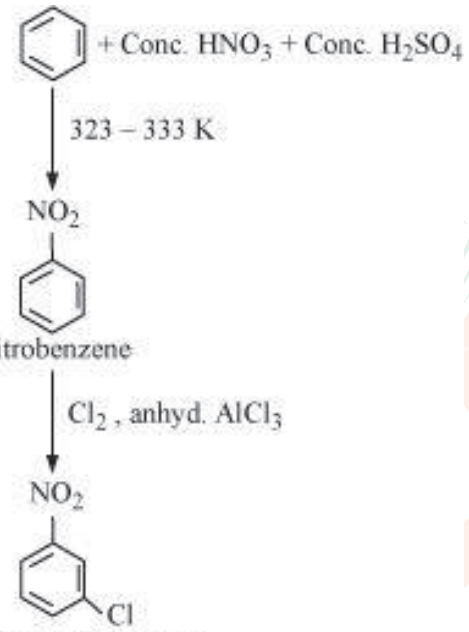
ANSWER:-

(i) Benzene can be converted into p-nitrobromobenzene as:



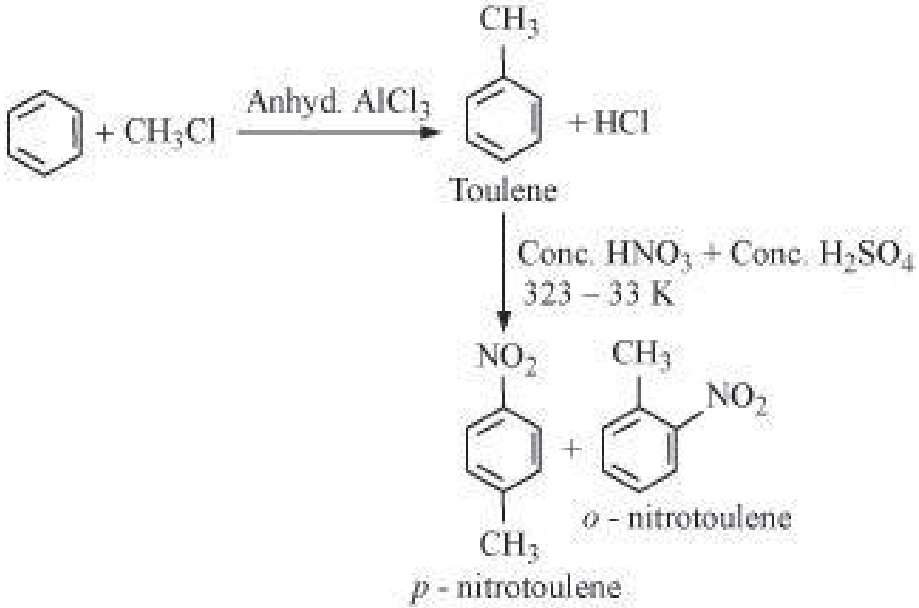
p - nitrobromobenzene

(ii) Benzene can be converted into m-nitrochlorobenzene as:



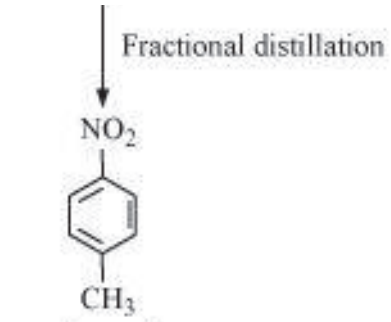
m - chloronitrobenzene

(iii) Benzene can be converted into p-nitrotoulene as:



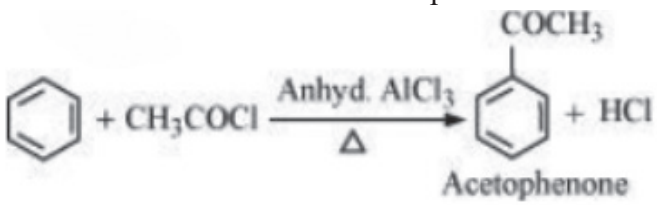
o - nitrotoulene

p - nitrotoulene



p - nitrotoulene

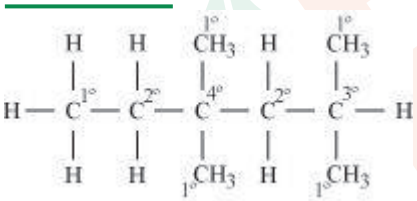
(iv) Benzene can be converted into acetophenone as:



Acetophenone

Q. 14. **In the alkane $H_3C–CH_2–C(CH_3)_2–CH_2–CH(CH_3)_2$, identify 1°, 2°, 3° carbon atoms and give the number of H atoms bonded to each one of these.**

ANSWER:-



- **Primary (1°) carbon atoms** are those bonded to only one other carbon atom, meaning they have a single carbon as their neighbour. In the given structure, there are **five** primary carbon atoms, each bonded to a total of **fifteen hydrogen atoms**.
- **Secondary (2°) carbon atoms** are bonded to **two** other carbon atoms, having two neighbouring carbons. The given structure contains **two** secondary carbon atoms, each associated with a total of **four hydrogen atoms**.
- **Tertiary (3°) carbon atoms** are bonded to **three** other carbon atoms, with three neighbouring carbons. The given structure has **one** tertiary carbon atom, which is attached to **only one hydrogen atom**.

Q. 15. **What effect does branching of an alkane chain has on its boiling point?**

ANSWER:-

Alkanes exhibit intermolecular Van der Waals forces, which influence their boiling points—the stronger the forces, the higher the boiling point.

As branching increases, the molecular surface area decreases, leading to a smaller area of contact between molecules. This reduction in surface interaction weakens the Van der Waals forces, making

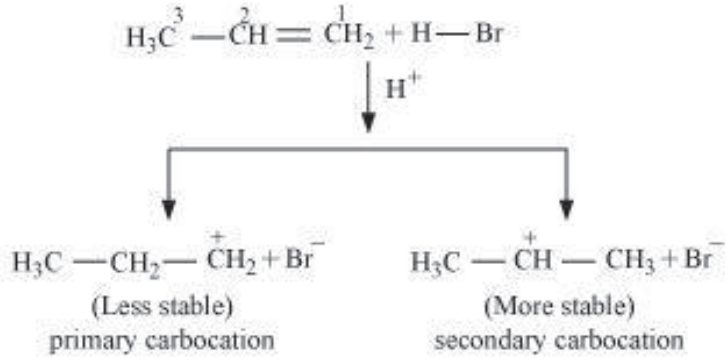
them easier to overcome at lower temperatures. Consequently, the boiling point of alkanes decreases as branching increases.

Q. 16. Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism.

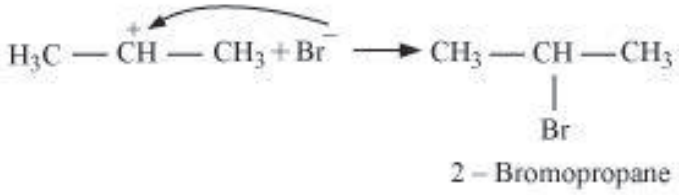
ANSWER:-

Addition of HBr to propene is an example of an electrophilic addition reaction.

Hydrogen bromide provides an electrophile, H^+. This electrophile attacks the double bond to form 1° and 2° carbocations as shown:

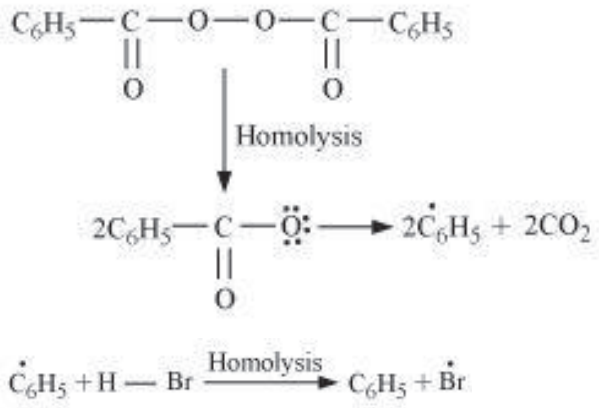


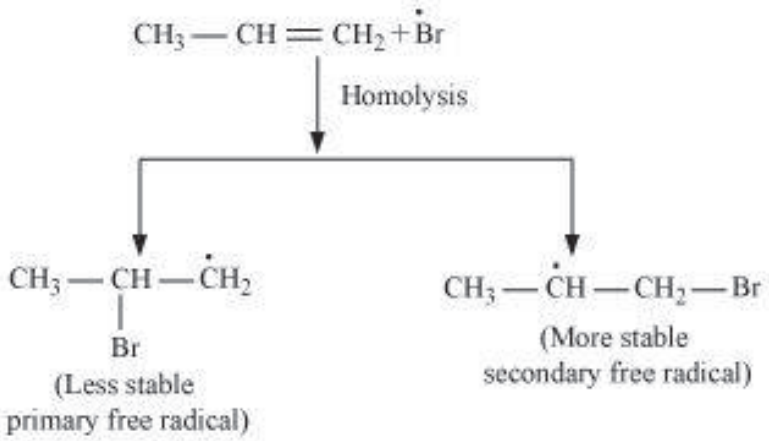
Secondary carbocations are more stable than primary carbocations. Hence, the former predominates since it will form at a faster rate. Thus, in the next step, Br^- attacks the carbocation to form 2 – bromopropane as the major product.



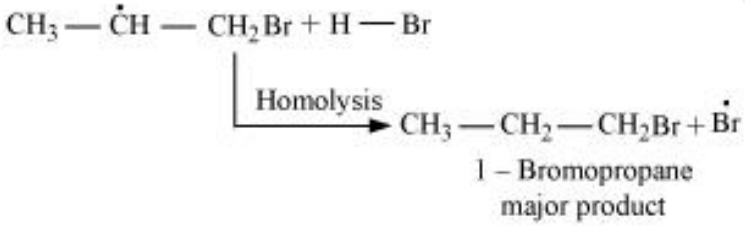
This reaction follows **Markovnikov's rule** where the negative part of the addendum is attached to the carbon atom having a lesser number of hydrogen atoms.

In the presence of benzoyl peroxide, an addition reaction takes place anti to Markovnikov's rule. The reaction follows a free radical chain mechanism as:





Secondary free radicals are more stable than primary radicals. Hence, the former predominates since it forms at a faster rate. Thus, 1 – bromopropane is obtained as the major product.

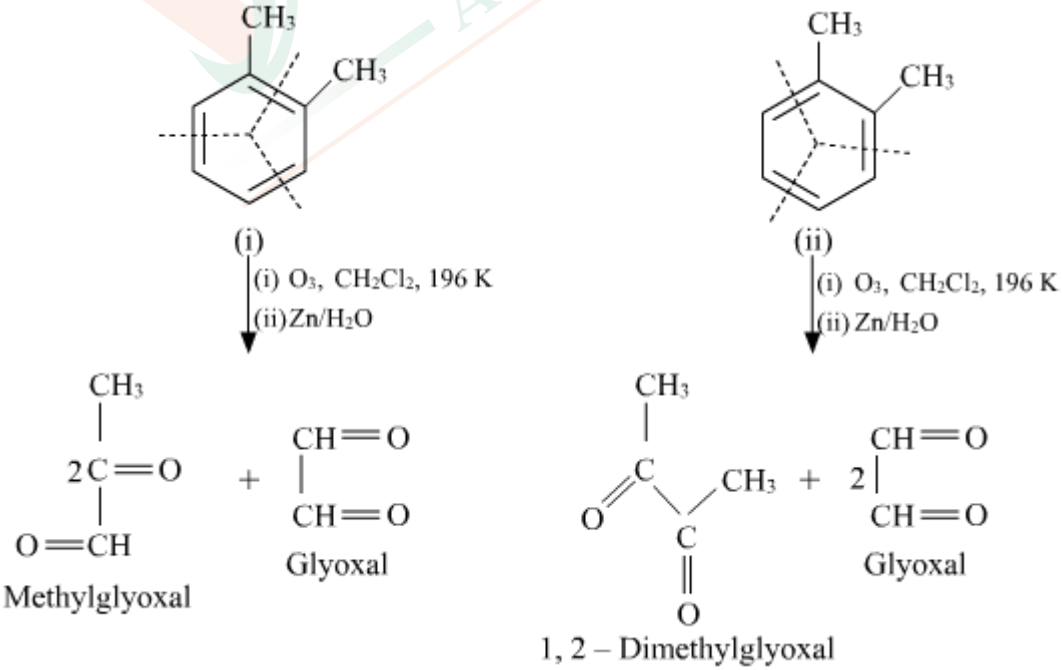


In the presence of peroxide, Br free radical acts as an electrophile. Hence, two different products are obtained on addition of HBr to propene in the absence and presence of peroxide.

Q. 17. 7 Write down the products of ozonolysis of 1, 2-dimethylbenzene (o-xylene). How does the result support Kekulé structure for benzene?

ANSWER:-

o-xylene has two resonance structures:



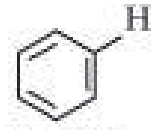
All three products, i.e., methyl glyoxal, 1, 2-dimethylglyoxal, and glyoxal are obtained from two Kekule structures. Since all three products cannot be obtained from any one of the two structures, this proves that o-xylene is a resonance hybrid of two Kekule structures (I and II).

Q. 18. Arrange benzene, n-hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behaviour.

ANSWER:-

Acidic character of a species is defined on the basis of ease with which it can lose its H–atoms.

The hybridization state of carbon in the given compound is:



Benzene
sp^2

Hexane
sp^3

Ethyne
sp

As the s–character increases, the electronegativity of carbon increases and the electrons of C–H bond pair lie closer to the carbon atom. As a result, partial positive charge of H–atom increases and H^+ ions are set free.

The s–character increases in the order:

$sp^3 < sp^2 < sp$

Hence, the decreasing order of acidic behaviour is Ethyne > Benzene > Hexane.

Q. 19. Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?

ANSWER:-

Benzene is a planar aromatic molecule with a delocalized π-electron cloud above and below the plane of the ring, making it electron-rich. As a result, it readily attracts electron-deficient species (electrophiles) and predominantly undergoes electrophilic substitution reactions.

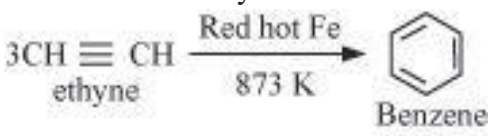
Conversely, nucleophiles, being electron-rich, are repelled by benzene, making nucleophilic substitution reactions difficult to occur.

Q. 20. How would you convert the following compounds into benzene?

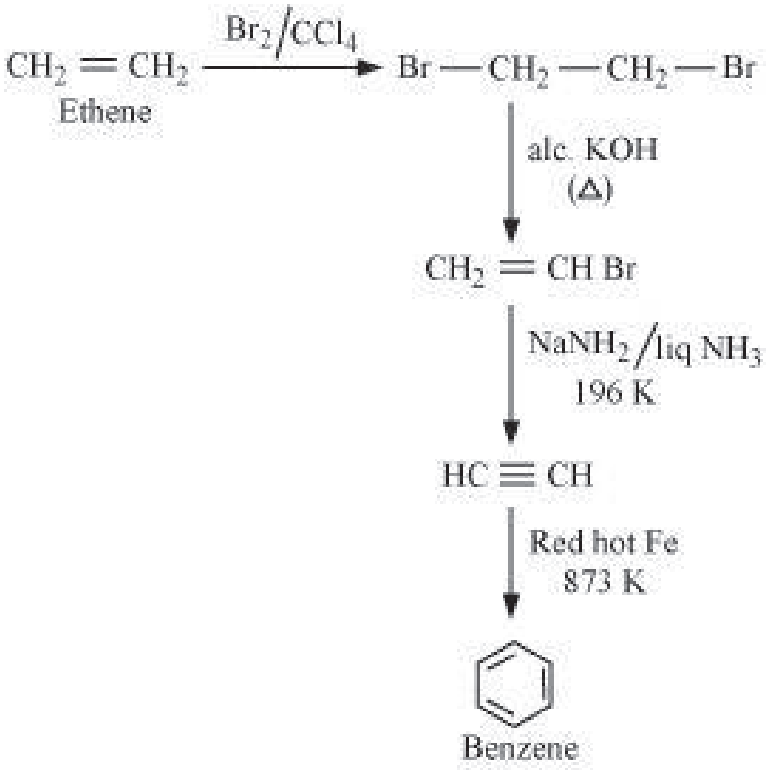
(i) Ethyne **(ii) Ethene** **(iii) Hexane**

ANSWER:-

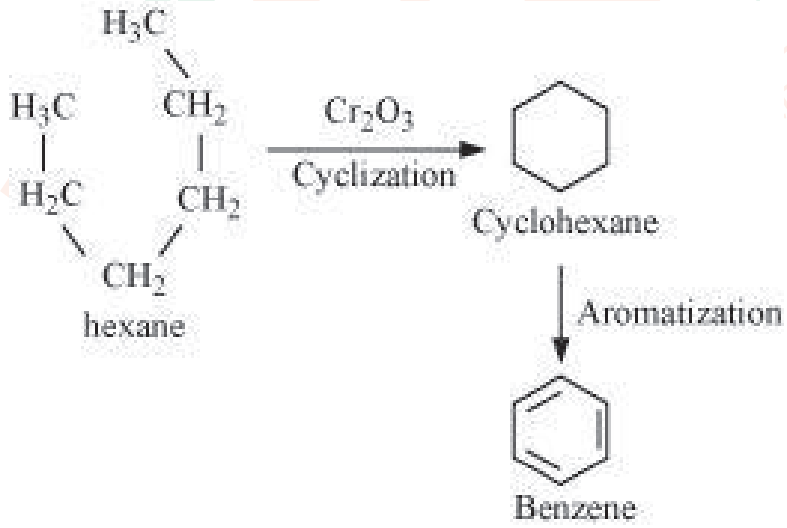
(i) Benzene from Ethyne:



(ii) Benzene from Ethene:



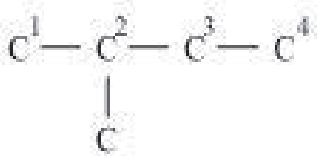
(iii) Hexane to Benzene



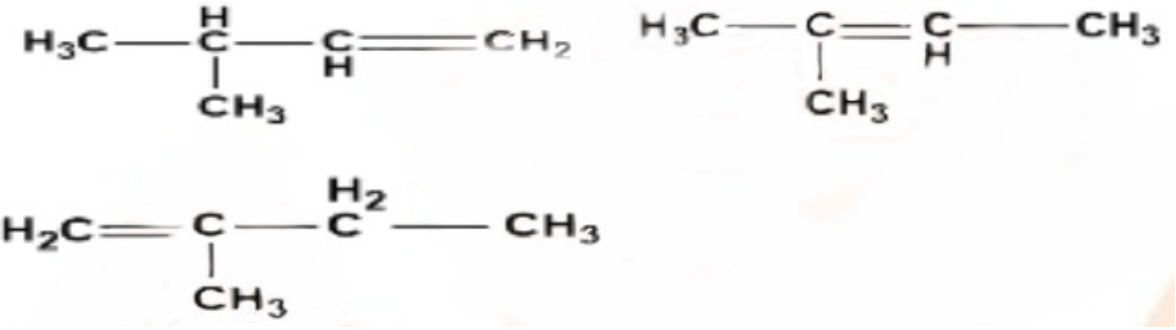
Q. 21. Write structures of all the alkenes which on hydrogenation give 2-methylbutane.

ANSWER:-

The basic skeleton of 2-methylbutane is shown below:



On the basis of this structure, various alkenes that will give 2-methylbutane on hydrogenation are:



Q. 22. Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+

(a) Chlorobenzene, 2,4-dinitrochlorobenzene, p-nitrochlorobenzene

(b) Toluene, p-$H_3C - C_6H_4 - NO_2$, p-$O_2N - C_6H_4 - NO_2$.

ANSWER:-

The higher the electron density on a benzene ring, the more reactive is the compound towards an electrophile, E+ (Electrophilic reaction).

(a) The presence of an electron withdrawing group (i.e., NO_2 and Cl^-) deactivates the aromatic ring by decreasing the electron density.

Since NO_2^- group is more electron withdrawing (due to resonance effect) than the Cl^- group (due to inductive effect), the decreasing order of reactivity **is as follows:**

Chlorobenzene > p – nitrochlorobenzene > 2, 4 – dinitrochlorobenzene

(b) While CH_3– is an electron donating group, NO_2– group is electron withdrawing. Hence, toluene will have the maximum electron density and is most easily attacked by E+.

NO_2– is an electron withdrawing group. Hence, when the number of NO_2– substituents is greater, the order is as follows:

Toluene > p– CH_3–C_6H_4 – NO_2, p –O_2 N– C_6H_4 – NO_2

Q. 23. Out of benzene, m–dinitrobenzene and toluene which will undergo nitration most easily and why?

ANSWER:-

The ease of nitration depends on the electron density available on the aromatic ring to facilitate the formation of nitro compounds. Nitration is an electrophilic substitution reaction, where the electron-rich benzene ring is attacked by the nitronium ion (NO_2^+).

In this context, the –CH_3 (methyl) group is an electron-donating group (EDG), increasing the electron density on the ring, while the –NO_2 (nitro) group is an electron-withdrawing group (EWG), reducing electron density. As a result, toluene has the highest electron density among the given compounds, followed by benzene. In contrast, m-dinitrobenzene, with two strongly withdrawing –NO_2 groups, has the lowest electron density, making nitration more difficult.

Thus, the increasing order of nitration is:

m-Dinitrobenzene < Benzene < Toluene

Q. 24. Suggest the name of a Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene.

ANSWER:-

The ethylation reaction of benzene involves the addition of an ethyl group on the benzene ring. Such a reaction is called a Friedel-Craft alkylation reaction. This reaction takes place in the presence of a Lewis acid.

Any Lewis acid like anhydrous $FeCl_3$, $SnCl_4$, BF_3 etc. can be used during the ethylation of benzene.

Q. 25. Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example.

ANSWER:-

Wurtz reaction is limited for the synthesis of symmetrical alkanes (alkanes with an even number of carbon atoms) In the reaction, two similar alkyl halides are taken as reactants and an alkane, containing double the number of carbon atoms, are formed. Example:

$$\underset{\text{Bromomethane}}{CH_3-Br} + 2Na + Br-CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3-CH_3} + 2NaBr$$

Wurtz reaction cannot be used for the preparation of unsymmetrical alkanes because if two dissimilar alkyl halides are taken as the reactants, then a mixture of alkanes is obtained as the products. Since the reaction involves free radical species, a side reaction also occurs to produce an alkene.

Example:

$$\underset{\text{Iodomethane}}{H_3C-I} + 2Na + \underset{\text{Iodoethane}}{I-CH_2-CH_3} \xrightarrow{\text{Dry ether}} \underset{\text{Propane}}{H_3C-CH_2CH_3} + 2NaI$$

$$H_3C-I + 2Na + I-CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{H_3C-CH_3} + 2NaI$$

$$H_3C-CH_2-I + 2Na + I-CH_2-CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Butane}}{H_3CH_2C-CH_2CH_3} + 2NaI$$