Question 13.1:
How do you account for the formation of ethane during chlorination of methane?
Answer 13.1: The methane chlorination process works through a free radical chain mechanism.

Step 1: Initiation:

The result begins with the hemolytic cleavage of Cl – Cl bond as:

$$Cl-Cl \longrightarrow \dot{Cl} + \dot{C}$$

Step 2: Propagation:

In this propagation step, chlorine-free radicals attack methane molecules and the C-H bond collapses to form methyl radicals as:

$$CH_4 + \dot{Cl} \longrightarrow CH_3 + H-Cl$$

When these methyl radicals react with other chlorine-free radicals, methyl chloride is formed next to the liberation of a chlorine-free radical.

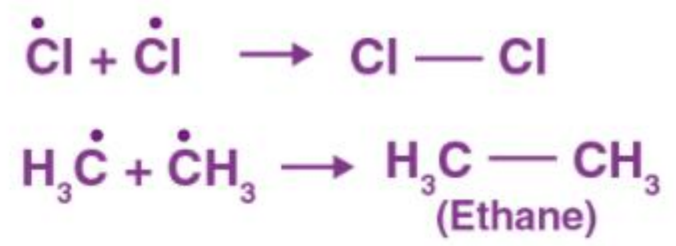
$$\dot{C}H_3 + Cl-Cl \longrightarrow \underset{\text{Methyl chloride}}{CH_3-Cl} + \dot{Cl}$$

$$CH_3Cl + \dot{Cl} \longrightarrow \dot{C}H_2Cl + HCl$$

$$\dot{C}H_2Cl + Cl-Cl \longrightarrow CH_2Cl_2 + \dot{Cl}$$

Step 3: Termination:

Ethane formation is the result of the termination of the chain reactions resulting from the ingestion of reactants as:



Through this process, ethane is thus obtained as a by-product of methane chlorination.

Question 13.2:

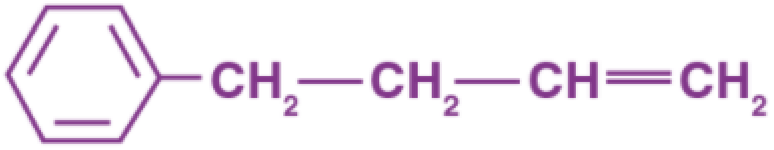
Write the IUPAC names of the following compounds:

(i) CH_3 CH = C $(CH_3)_2$

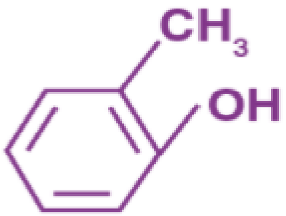
(ii) CH_2 = CH – C C – CH_3

(iii)

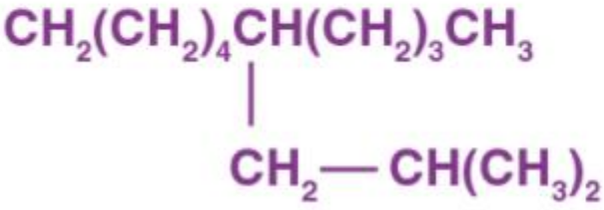
(iv)



(v)

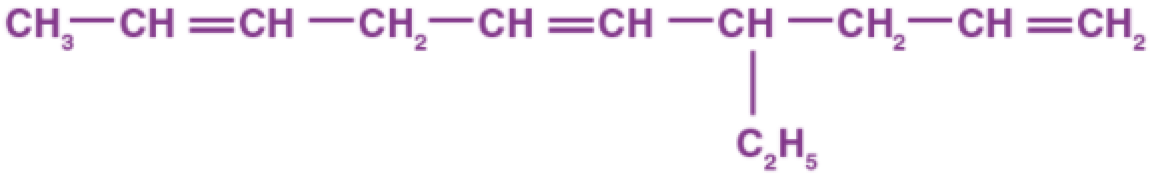


(vi)



$$\begin{array}{l} CH_2(CH_2)_4\underset{|}{C}H(CH_2)_3CH_3 \\ \qquad\qquad\quad CH_2-CH(CH_3)_2 \end{array}$$

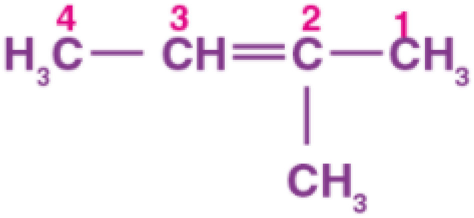
(vii)



$$CH_3-CH=CH-CH_2-CH=CH-\underset{\substack{|\\ C_2H_5}}{CH}-CH_2-CH=CH_2$$

Answer 13.2:

(i)



$$H_3\overset{4}{C}-\overset{3}{C}H=\underset{\substack{|\\ CH_3}}{\overset{2}{C}}-\overset{1}{C}H_3$$

2-Methylbut-2-ene is the required IUPAC name

(ii)

$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{C}\equiv\overset{4}{C}-\overset{5}{CH_3}$

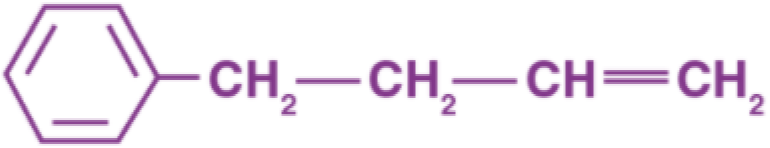
Pen-1-ene-3-yne is the required IUPAC name

(iii)

1, 3-Butadiene or Buta-1,3-diene is the required IUPAC name

$\overset{1}{H_2C}=\overset{2}{CH}-\overset{3}{CH}=\overset{4}{CH_2}$

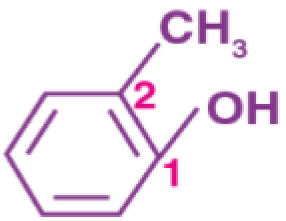
(iv)



$C_6H_5-CH_2-CH_2-CH=CH_2$

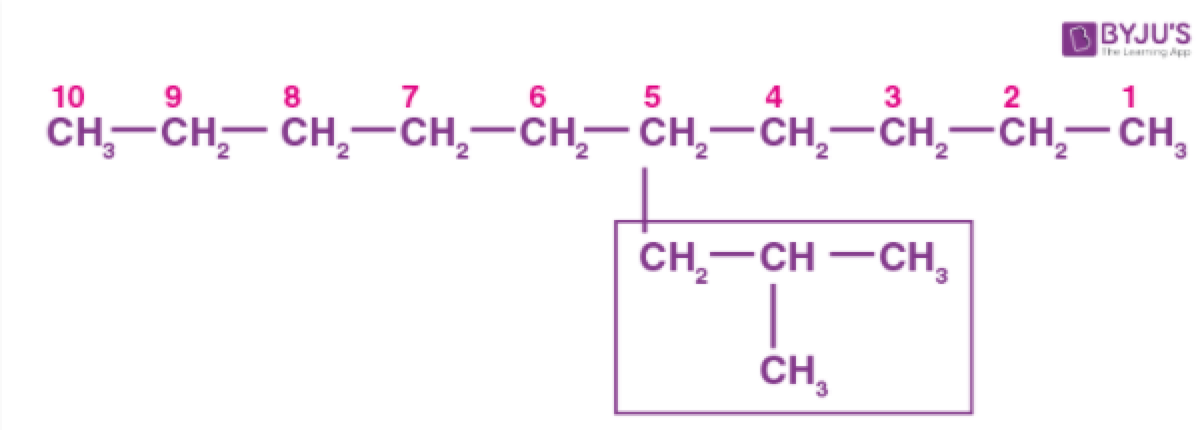
4-Phenyl but-1-ene is the required IUPAC name

(v)



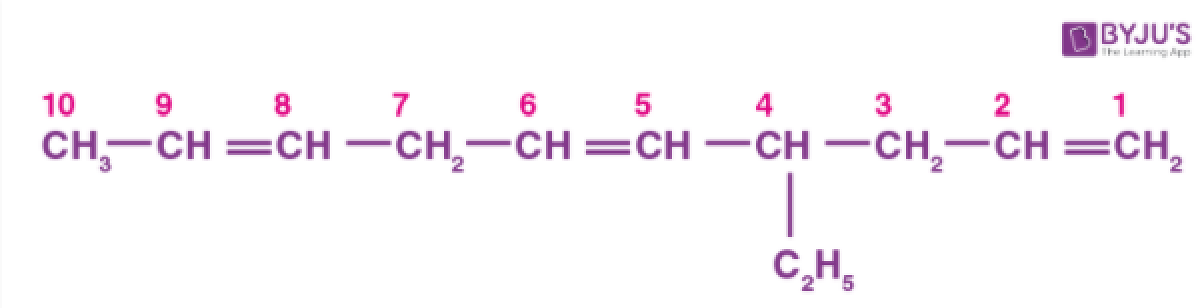
2-Methyl phenol is the required IUPAC name

(vi)



5-(2-Methylpropyl)-decane is the required IUPAC name

(vii)



$$\overset{10}{CH_3}-\overset{9}{CH}=\overset{8}{CH}-\overset{7}{CH_2}-\overset{6}{CH}=\overset{5}{CH}-\underset{C_2H_5}{\overset{4}{CH}}-\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}$$

4-Ethyldeca-1, 5, 8-triene is the required IUPAC name

Question 13.3:

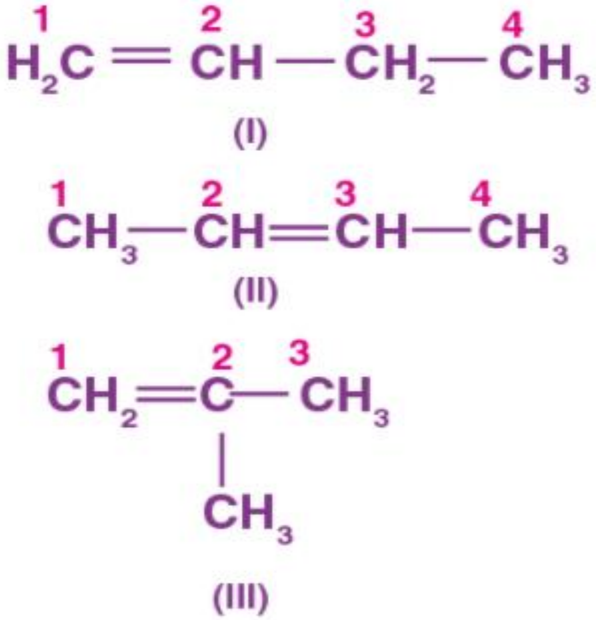
For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of the double or triple bond as indicated:

(a) C_4H_8 (one double bond)

(b) C_5H_8 (one triple bond)

Answer 13.3:

(a) The resulting structural isomers with one double bond are probable for C_4H_8:



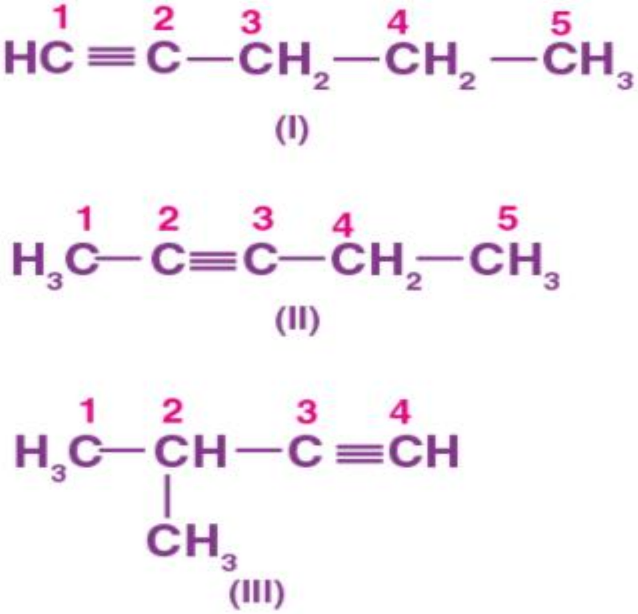
The IUPAC name of

Compound (I) is But-1-ene,

Compound (II) is But-2-ene, and

Compound (III) is 2-Methylprop-1-ene.

(b) The subsequent structural isomers are probable for C_5H_8 with one triple bond:



The IUPAC name of

Compound (I) is Pent-1-yne,

Compound (II) is Pent-2-yne, and

Compound (III) is 3-Methylbut-1-ene.

Question 13.4:

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

(i) Pent-2-ene

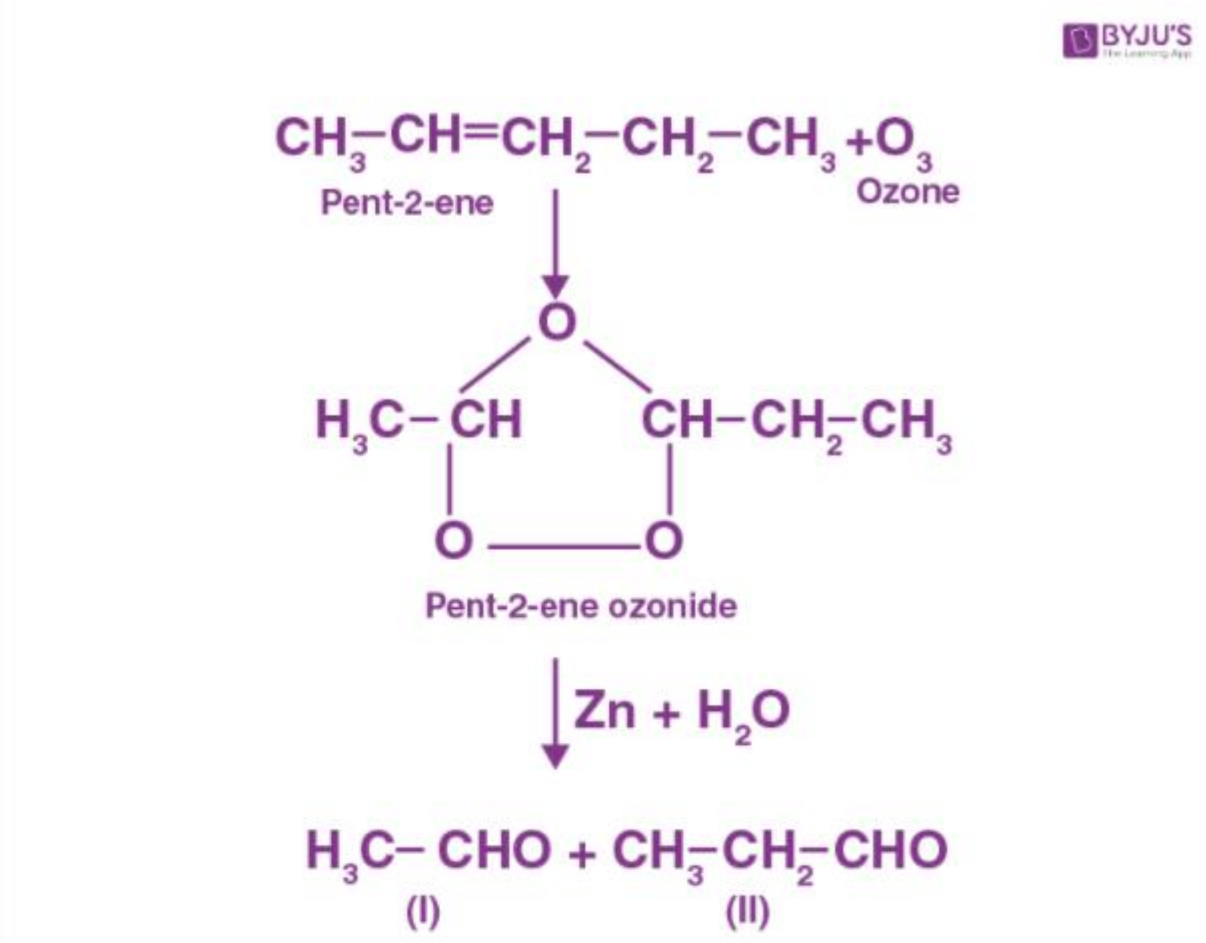
(ii) 3, 4 – Dimethyl-hept-3-ene

(iii) 2-Ethylbut-1-ene

(iv) 1 – Phenylbut-1-ene

Answer 13.4:

(i) Ozonolysis of Pent-2-ene is shown as:

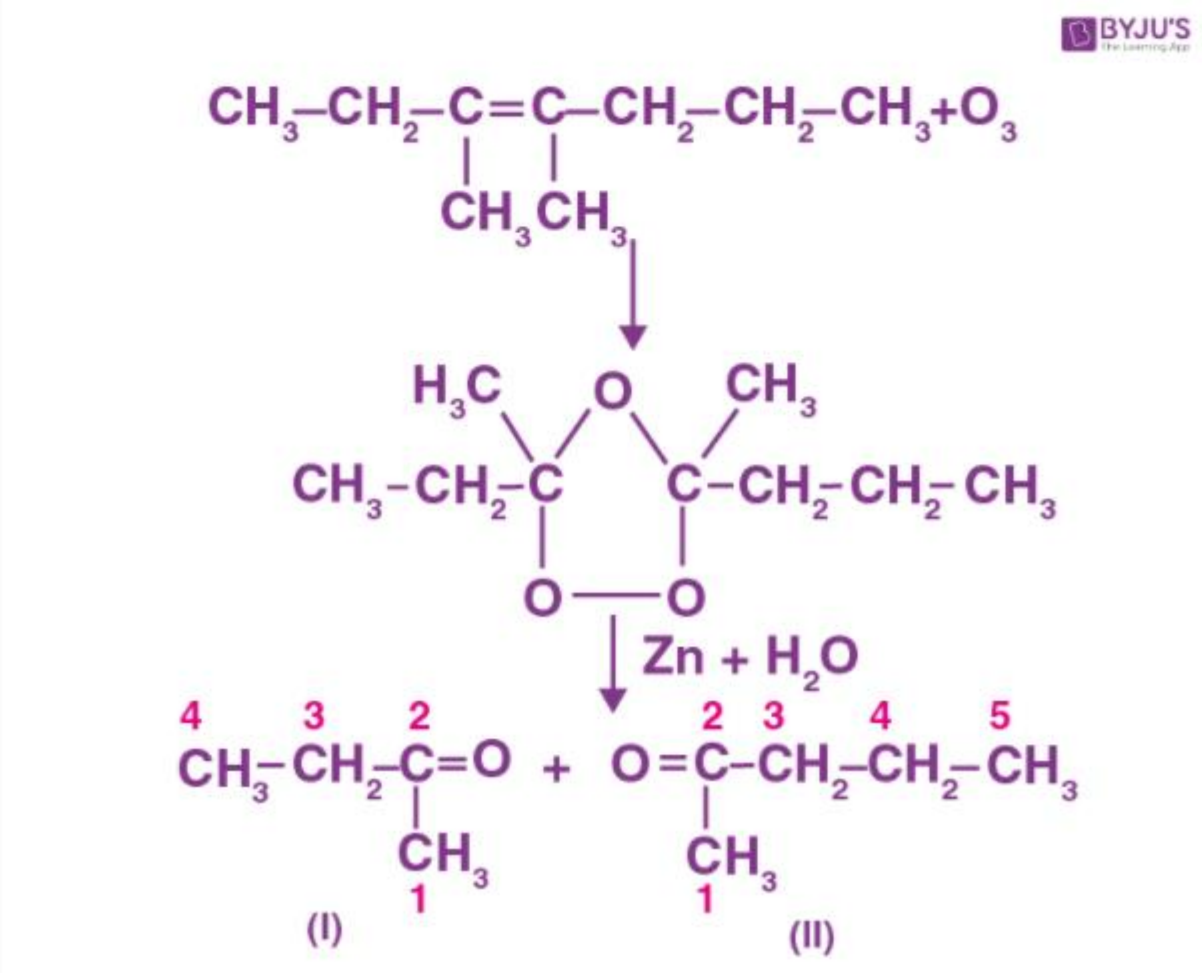


The following Product IUPAC names are:

Product (I) ethanal, and

Product (II) propanal.

(ii) Ozonolysis of 3, 4-Dimethylhept-3-ene is shown as:

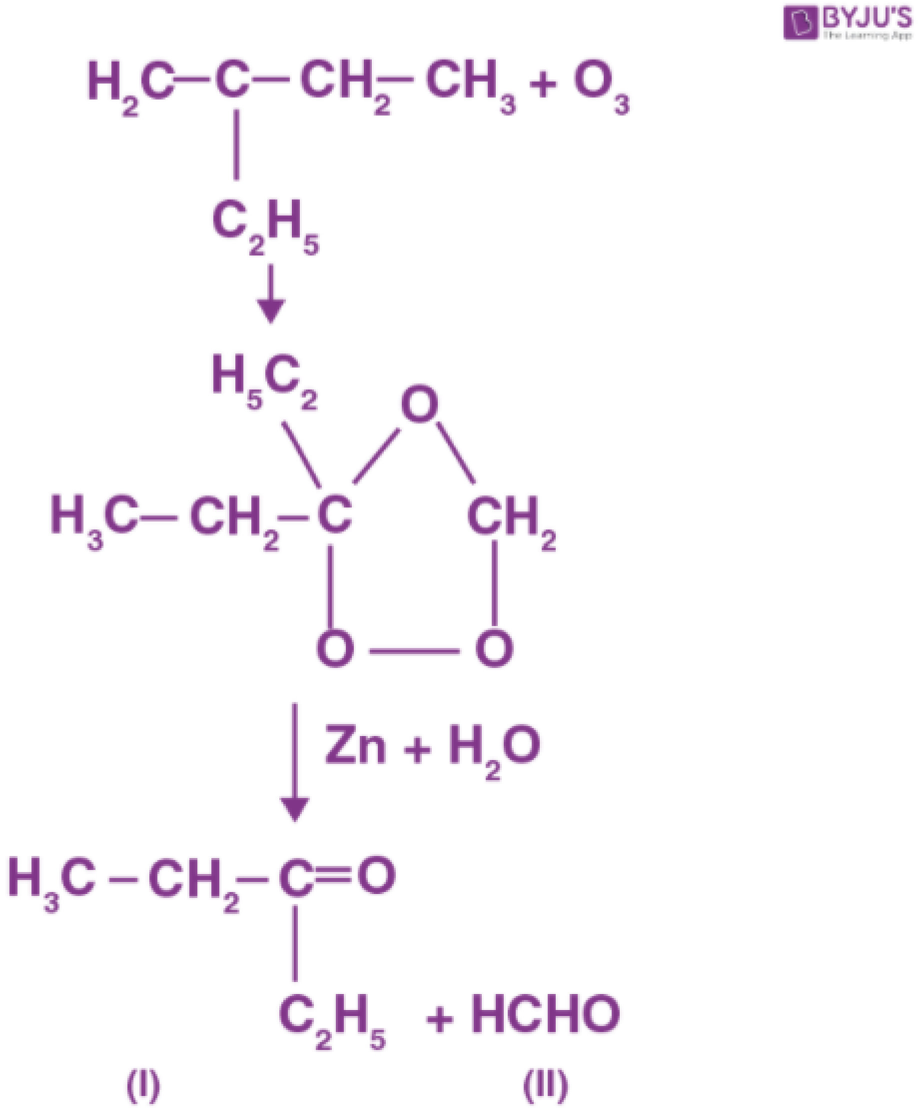


The product names subsequent to IUPAC are:

Product (I) butan-2-one, and

Product (II) Pentan-2-one

(iii) Ozonolysis of 2-Ethylbut-1-ene is shown as:

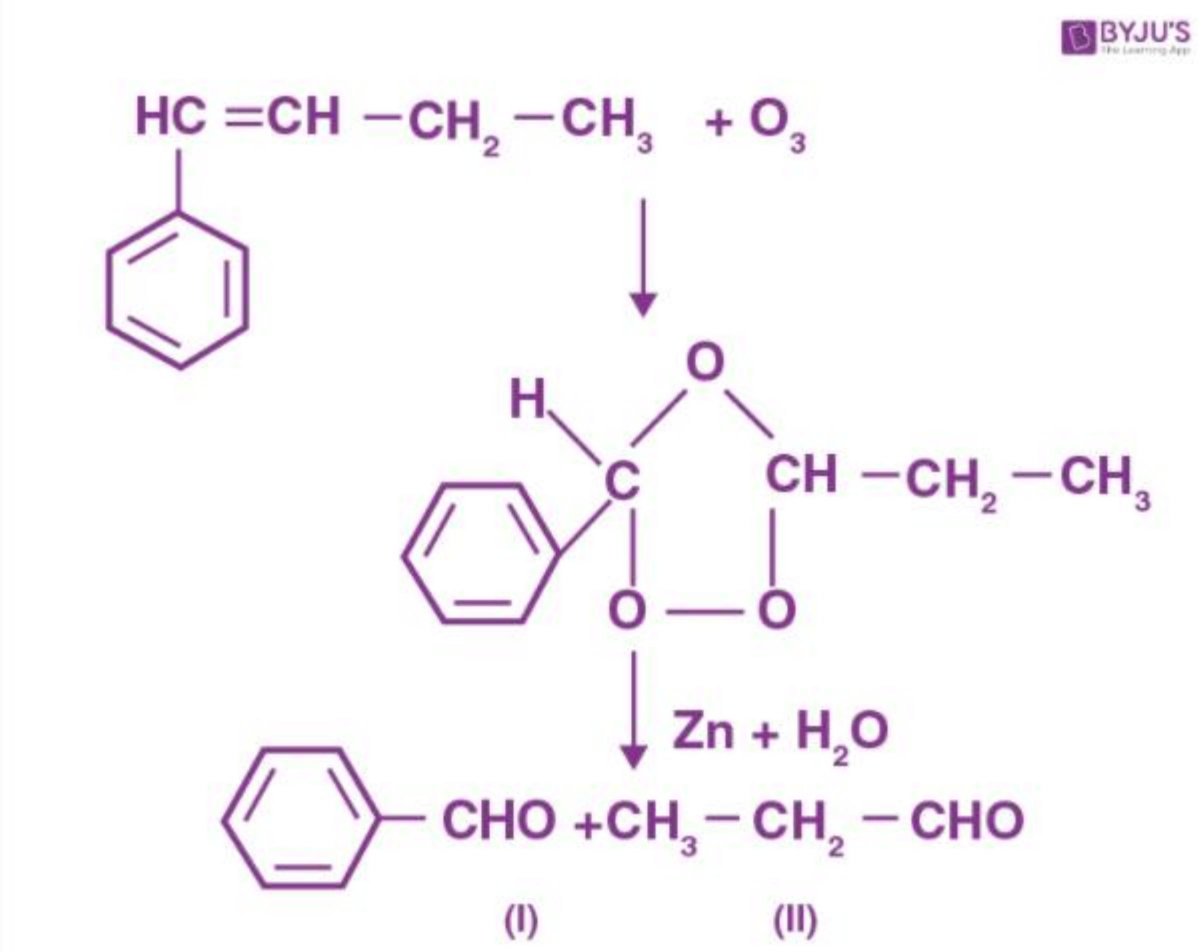


The subsequent IUPAC names of the products are:

Product (I) pentan-3-one, and

Product (II) methanal

(iv) Ozonolysis of 1 – Phenylbut-1-ene is shown as



The subsequent IUPAC names of the products are:

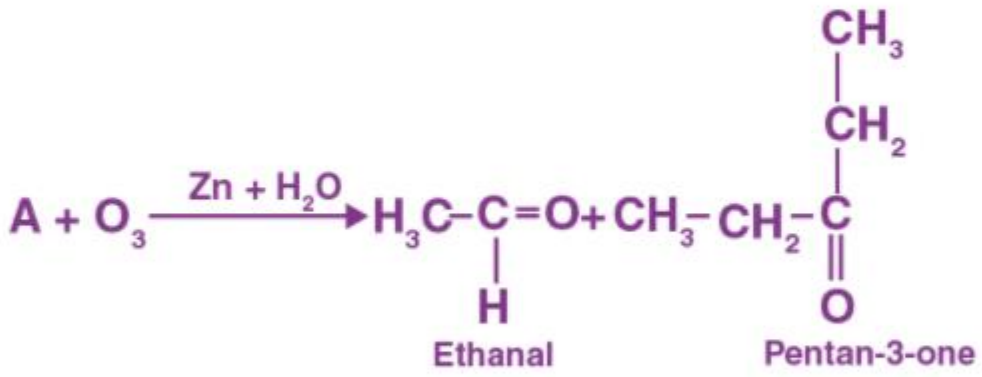
Product (I) benzaldehyde, and

Product (II) propanal

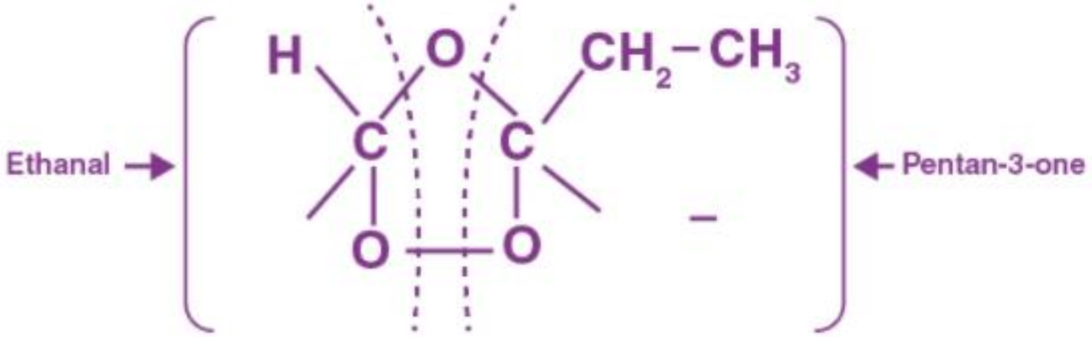
Question 13.5:

An alkene ‘A’ on ozonolysis gives a mixture of ethanal and pentan-3- one. Write structure and IUPAC name of ‘A’.

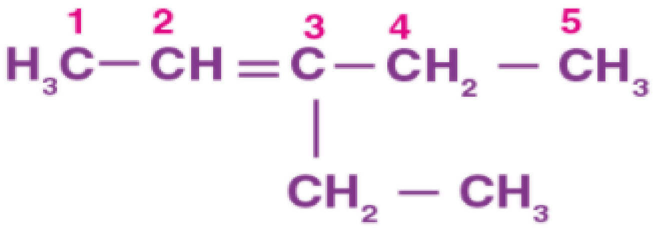
Answer 13.5:



In the course of ozonolysis, an ozonide is produced as an intermediate that has a cyclic structure; it undergoes cleavage to provide the final products. Ethanal and pentan-3-one are obtained from the ozonide intermediates. So, the possible ozonide structure will be:



This ozonide is produced by adding ozone to ‘A ‘as a transitional product that forms final products undergoing cleavage. The preferred ‘A ‘arrangement may be obtained by removing ozone from the ozonide. Therefore ‘A ”s structural formula is:



$$\overset{1}{H_3C}-\overset{2}{CH}=\overset{3}{C}(CH_2-CH_3)-\overset{4}{CH_2}-\overset{5}{CH_3}$$

As an outcome, ‘A’ is 3-Ethylpent-2-ene is the IUPAC name of alkene.

Question 13.6:

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'.

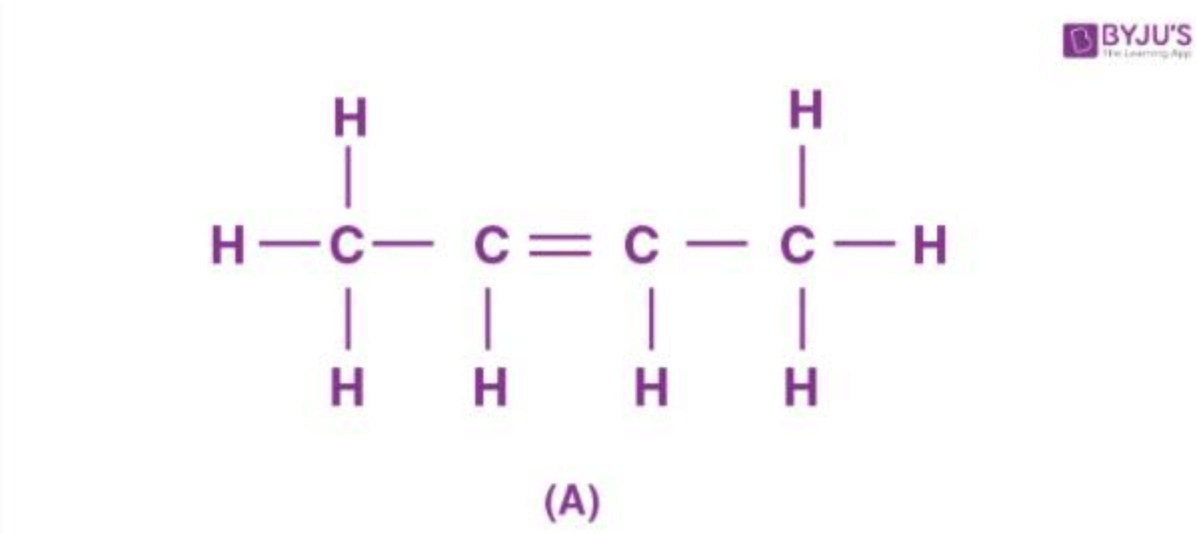
Answer 13.6:

From the information given it gives two moles of an aldehyde of molar mass 44 u when ' A ' undergoes ozonolysis. The formation of an aldehyde's two moles suggests that the presence of similar structural units on both sides of the C-C ÿ bond is present. Consequently, the ' A ' structure can be represented as shown below:

We know, XC = CX

Because there are eight C – H σ bonds, 8 hydrogen atoms are present in ' A. ' There are also three C – C bonds, so the ' A ' structure contains four carbon atoms.

The combination of all these inferences can represent the structure of ' A ' as shown below:



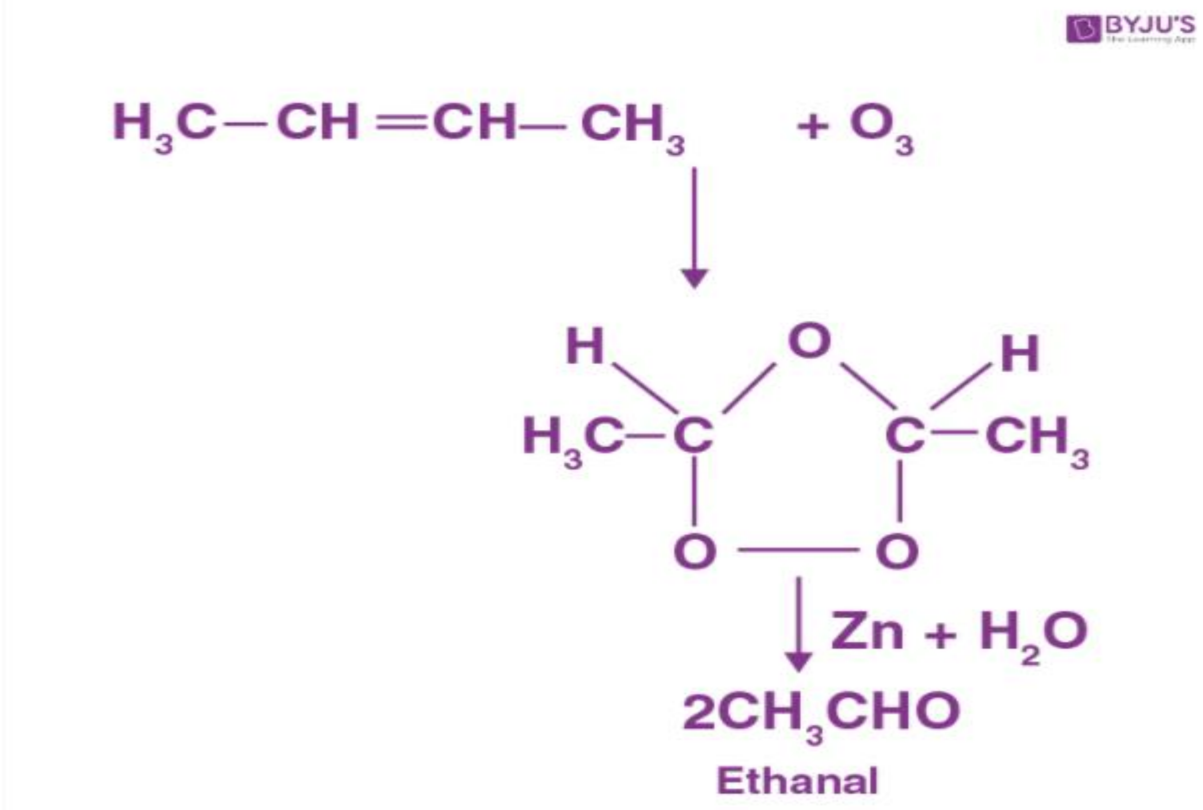
(A)

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

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

After Ozonolysis of 'A' takes place,

The end product is ethanol with molecular weight = 44 u



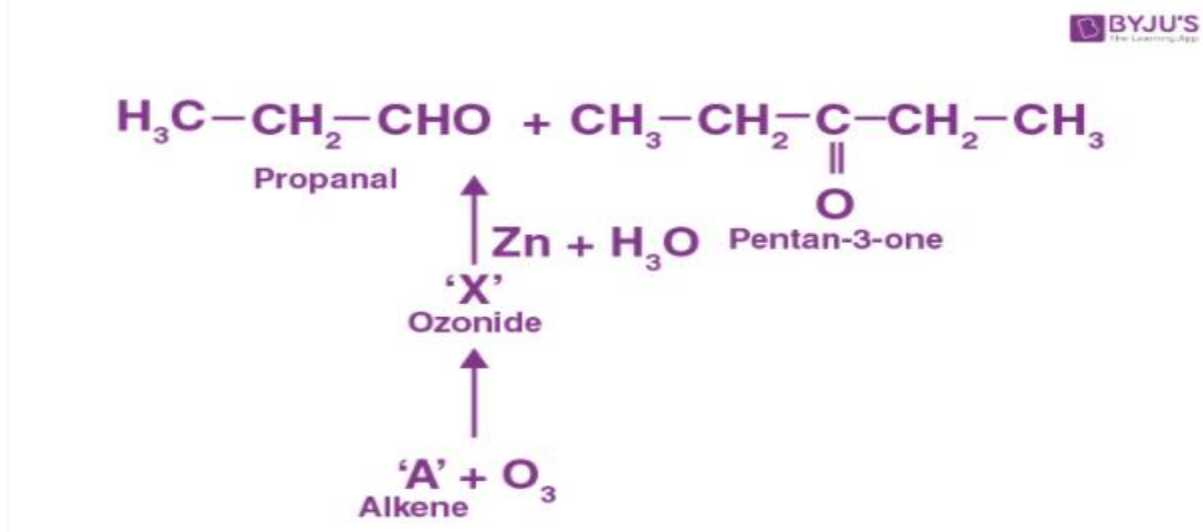
Question 13.7:

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

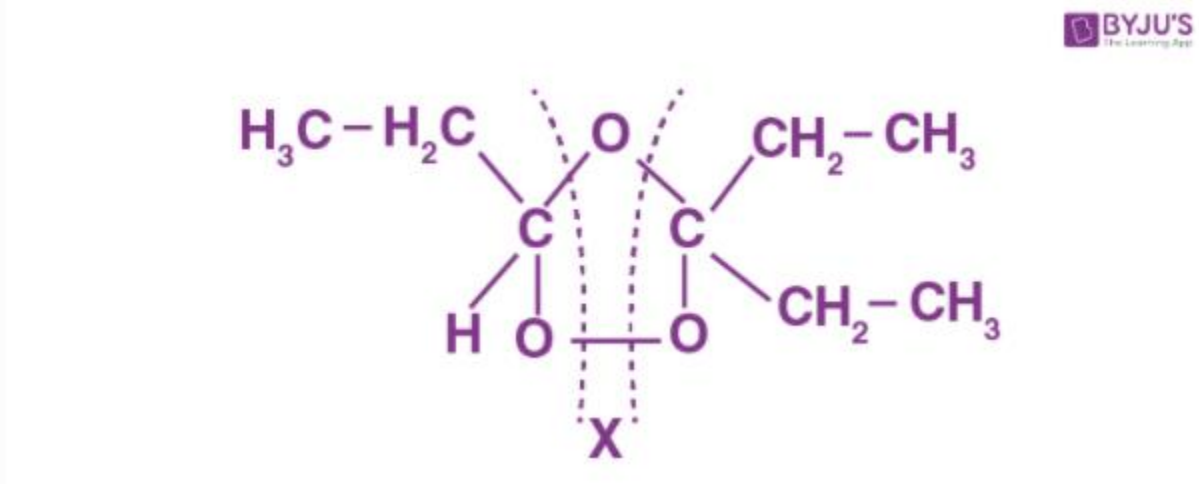
Answer 13.7:

From the given information, the two ozonolysis products of an alkene are pentan-3-one and propanal.

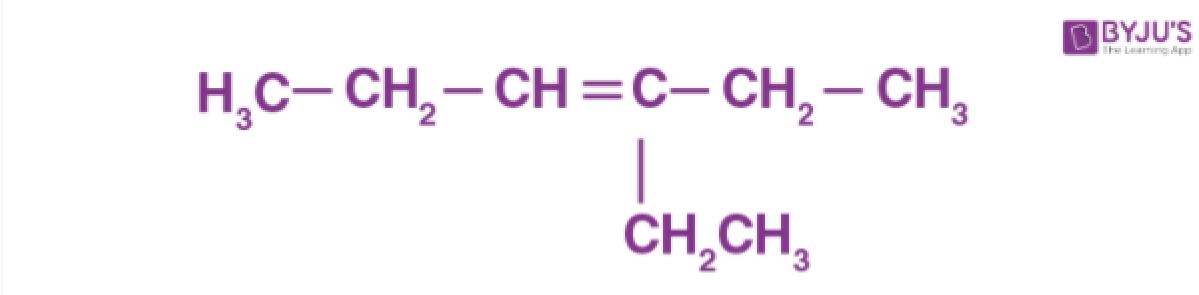
Suppose the alkene given is A. The reverse of the ozonolysis reaction is what we get,



The products obtained by ozonide cleavage, let it be ‘ X. ‘ Since ‘ X ‘ contains both products in cyclic form, the possible ozonide structure may be represented as shown below:



Because ‘ X ‘ is an additional component of the ozone alkene ‘ A. ‘ Therefore, the potential structure of the given ‘ A ‘ alkene will be:



$H_3C-CH_2-CH=C(CH_2CH_3)-CH_2-CH_3$

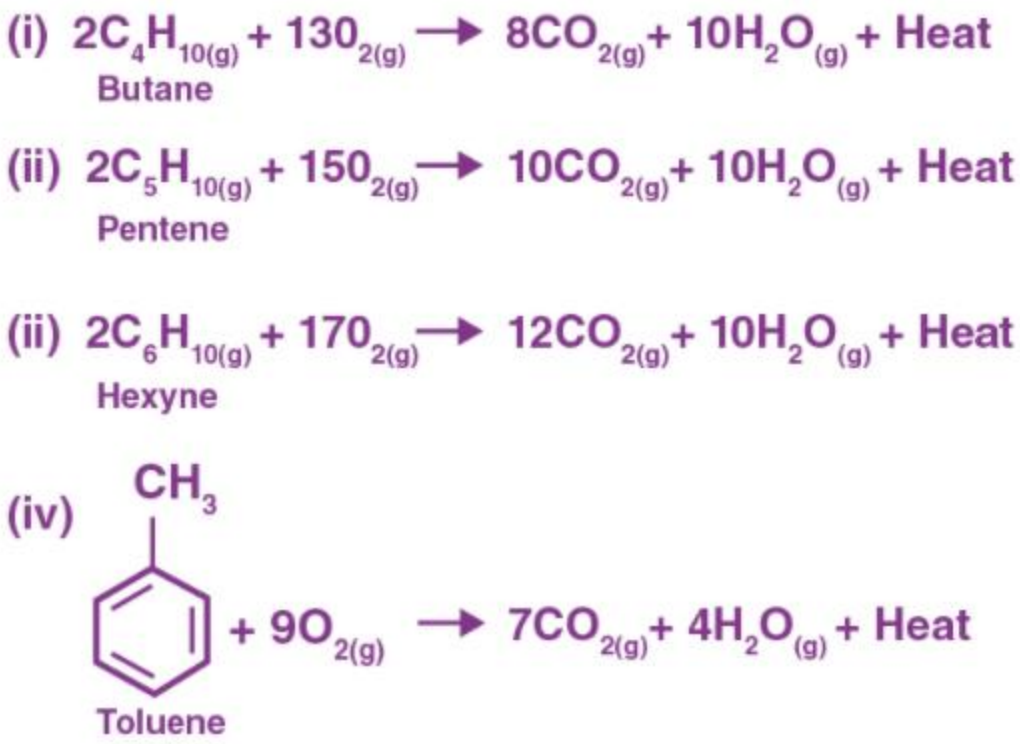
Question 13.8:

Write chemical equations for the combustion reaction of the following hydrocarbons:

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

Answer 13.8:

Combustion reactions may be defined as an oxygen or oxygen reaction of a compound.



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

Butane

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

Pentene

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

Hexyne

(iv) $+ 9O_{2(g)} \rightarrow 7CO_{2(g)} + 4H_2O_{(g)} + \text{Heat}$

Toluene

Question 13.9:

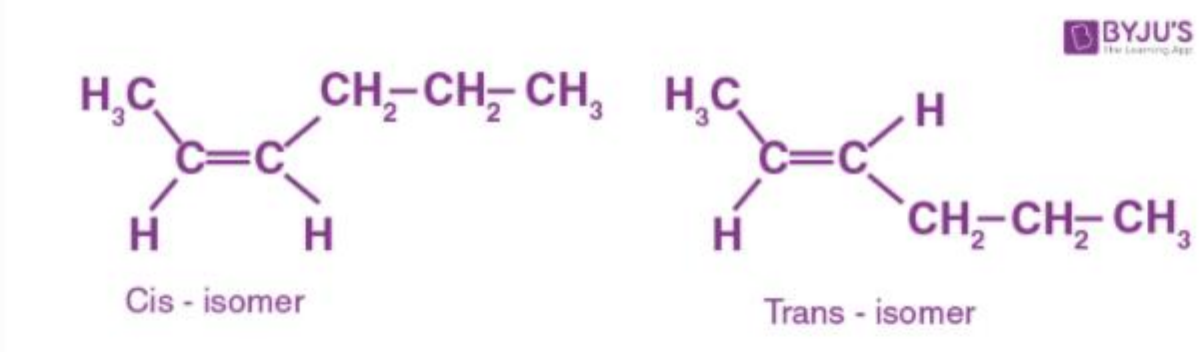
Draw the cis and trans structures of hex-2-ene. Which isomer will have higher b.p. and why?

Answer 13.9:

Hex-2-ene is represented as shown below:

$$H_3C-HC=CH-CH_2-CH_2-CH_3$$

Geometrical isomers of hex-2-ene are as follows:



A cis compounds dipole moment is equal to the sum of the C – CH_3 bond's dipole moments, and the C – CH $_2CH_3$ bonds that both act in the same direction.

On the other hand, a trans-compound dipole moment is the result of the dipole moments of C – CH_3 bonds and C – CH_2CH_3 bonds both acting in opposite directions

As cis-isomer is polar than trans-isomer. Thus, the higher the polarity, the greater the intermolecular dipole-dipole interaction and the need for more heat to break the bonds. The boiling will be higher, therefore.

Therefore, cis-isomer of a compound will have a higher boiling point than trans-isomer of that compound.

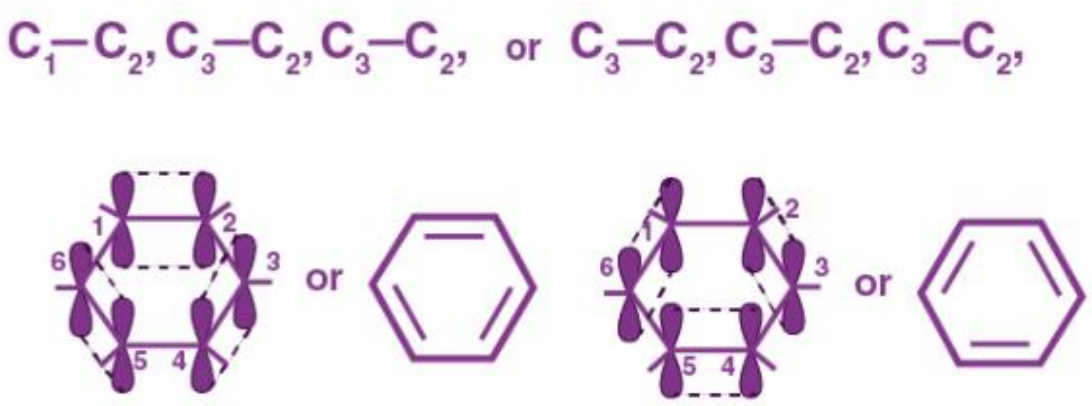
Question 13.10:

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

Answer 13.10:

Benzene is a hybrid of the resonating structures and it is shown as:

All six carbon atoms in benzene are hybridized to sp^2.In benzene, each carbon atom's two sp^2 hybrid orbital overlaps with its adjacent carbon atoms ' sp^2 hybrid orbital, forming a six-sigma bond in the hexagonal plane. The remaining hybrid orbital sp^2 on each carbon atom overlaps with the hydrogen atom's s-orbital to form six sigma C – H bonds. Now, the rest are unhybridized *p*-orbital of carbon atoms will have the possibility of forming three C-C π bonds by the lateral overlap of



These six π-bonds are delocalized and can move about the six-carbon nuclei freely. Therefore, due to the delocalization of these π-bonds, benzene is stabilized even after the presence of three C-C π -bonds.

Question 13.11:

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

Answer 13.11:

The essential conditions for any aromatic system are as follows:

(i) Firstly, the compound arrangement or structure should be planar.

(ii) The n-electrons are completely delocalized in the ring of a compound

(iii) The sum of n-electrons in the ring of a compound must be equal to (4n + 2)π,

Where n = 0, 1, 2, ….. and so on. This rule is called Huckel’s rule.

Question 13.12:

Explain why the following systems are not aromatic?

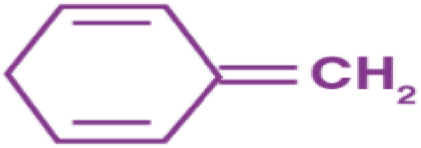
(i)

(ii)

(iii)

Answer 13.12:

(i)



Due to the presence of a sp^3-hybridized carbon, the system is not planar. It does contain six n-electrons but the system is not fully conjugated since all the six n-electrons do not form a single cyclic electron cloud that surrounds all the atoms of the ring. Therefore, it is not an aromatic compound.

(ii)

Due to the presence of sp^3– hybridized carbon, the system is not planar. Further, it contains only four n-electrons, therefore, the system is not aromatic because it does not contain planar cyclic cloud having (4n+2) n-electrons.

(iii)

Cyclo-octatetraene is not planar but is tub-shaped. It is, therefore, a non-planar system having 8 n-electrons. Therefore, the molecule is not aromatic as it does not contain a planar cyclic cloud having (4n + 2) n-electrons.

Question 13.13:

How will you convert benzene into:

(i) p – nitrobromobenzene

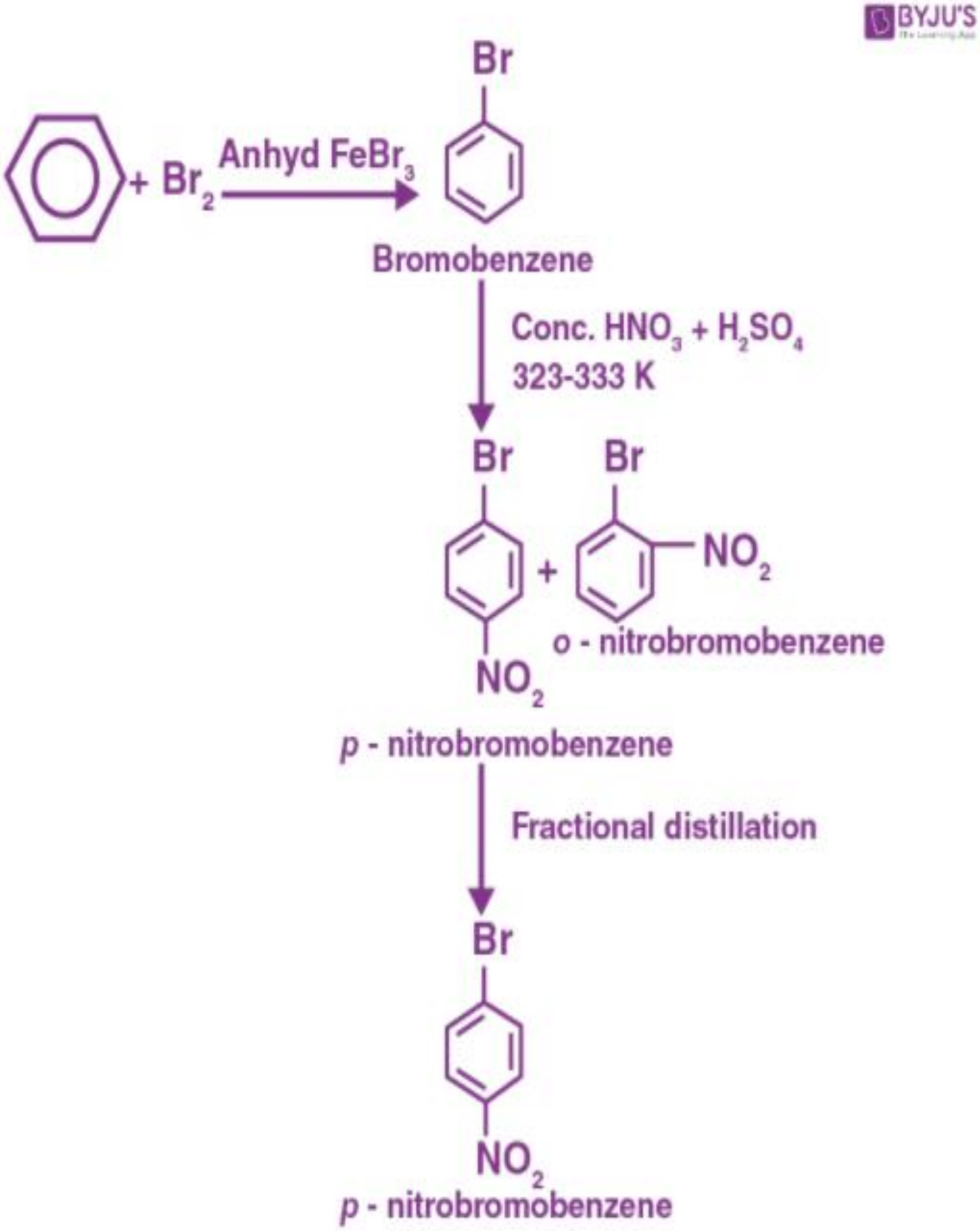
(ii) m-nitrochlorobenzene

(iii) p -nitrotoluene

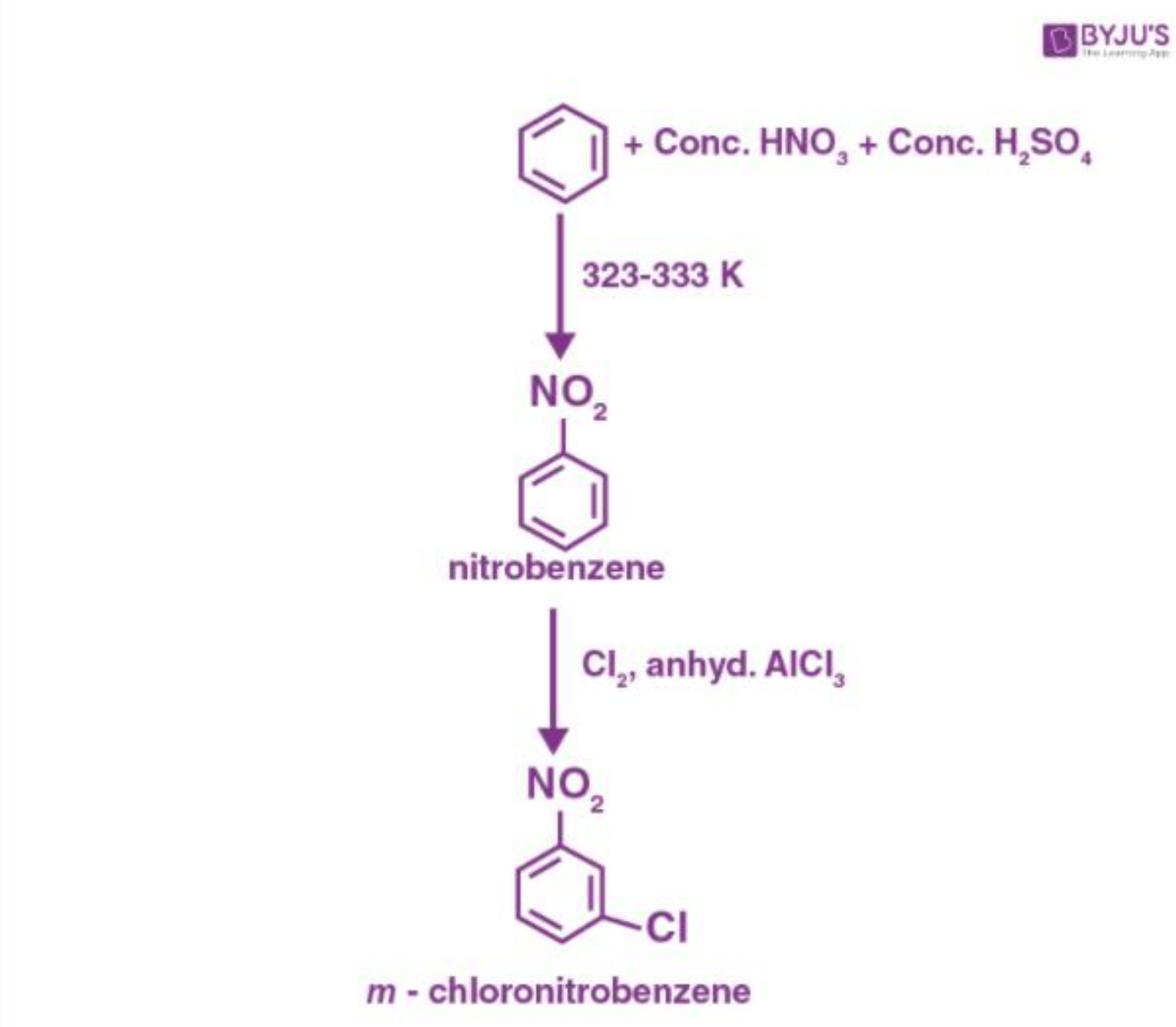
(iv) acetophenone

Answer 13.13:

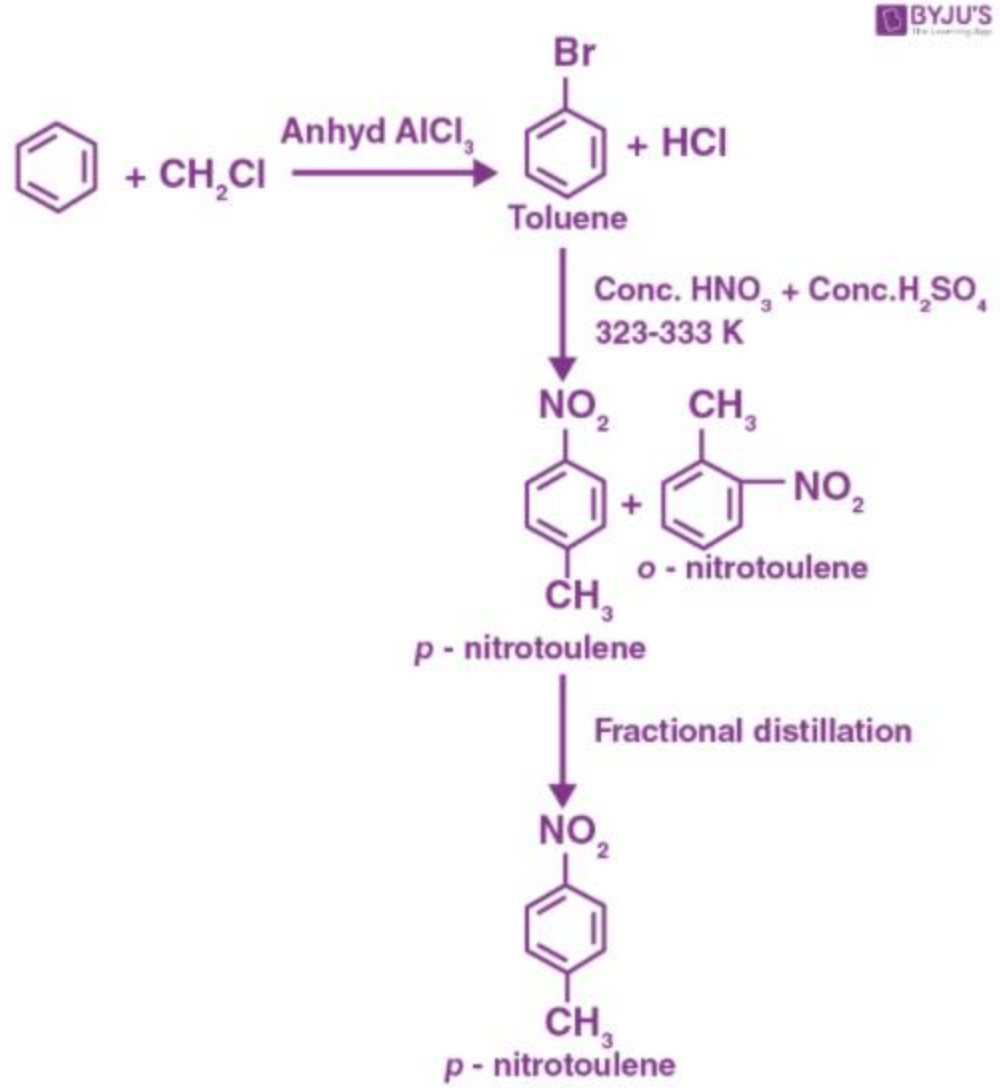
(i) Benzene converted to p – nitrobromobenzene



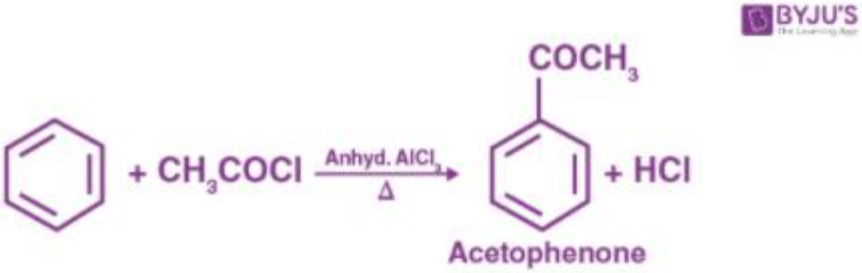
(ii) Benzene converted to m-nitrochlorobenzene



(iii) Benzene converted to p –nitrotoluene



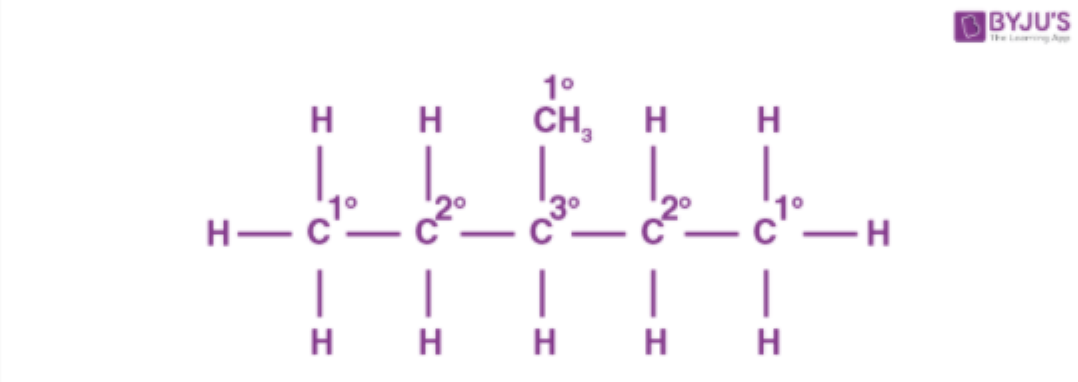
(iv) Benzene converted to acetophenone



Question 13.14:

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 13.14:



Primary carbon atoms (1°): Carbon atoms bonded to a single atom of carbon are called primary atoms of carbon. The arrangement given has corresponding five 1o carbon atoms and fifteen H atoms.

Secondary carbon atoms (2°): The secondary carbon atom is called carbon atom bonded to double carbon atom. The arrangement given has two corresponding 2o carbon atoms, and four H atoms.

Tertiary carbon atoms (3°): The term tertiary carbon atom is used to refer to carbon atoms bonded to three carbon atoms. The arrangement given has one corresponding 3 degree carbon atom and single H atom.

Question 13.15:

What effect does branching of an alkane chain has on its boiling point?

Answer 13.15:

Alkanes encounter Van-der Waals forces between molecules. The higher the alkane's power, the greater is the boiling point.

As the molecule branching increases, the surface area decreases which leads to a small contact area. As a result, the force of the Van-der Waals (or intermolecular force) decreases too. Those forces can be overcome very easily at a relatively lower temperature. Thus, the boiling point of an alkane chain decreases as branching increases.

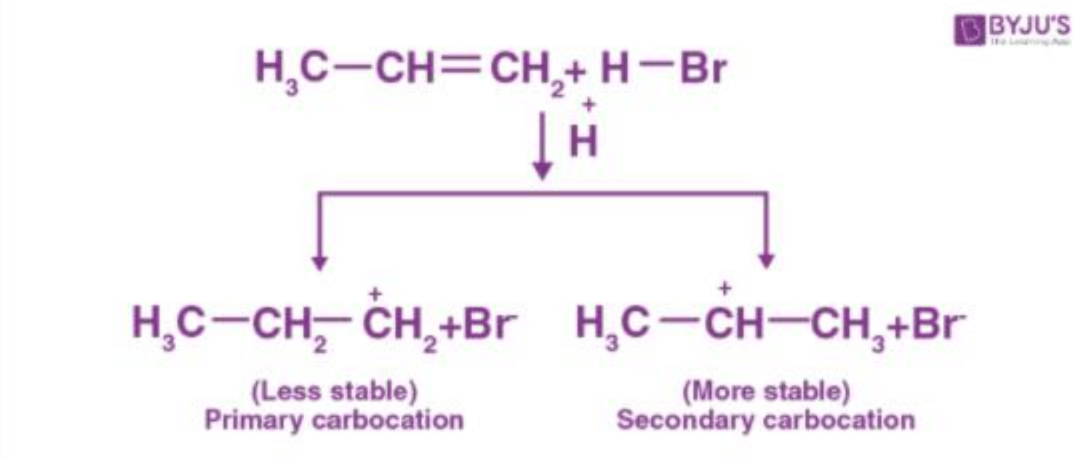
Question 13.16:

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 13.16:

The addition of HBr to propene is an example of an electrophilic substitution reaction.

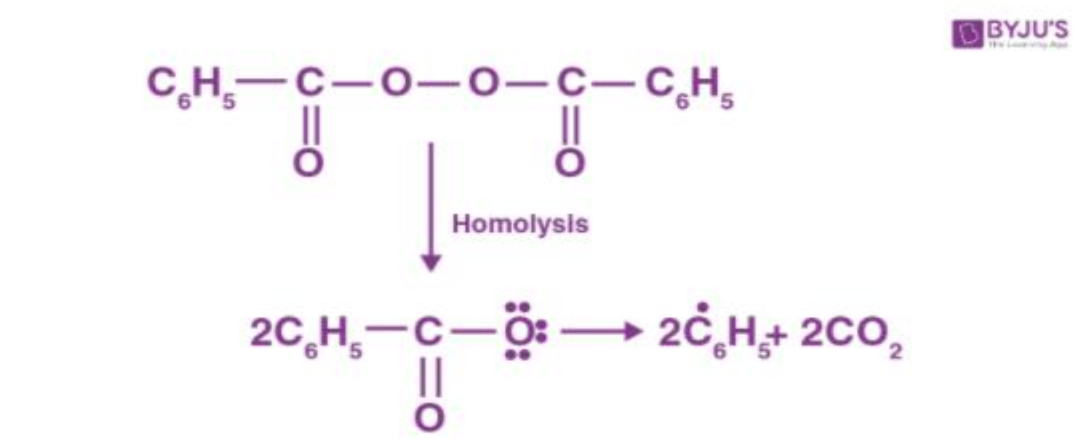
Being an acid, the hydrogen bromide provides an electrophile, H+. This electrophile attacks the propene double bond to form carbocations of 1 ° and 2 °, as shown below:

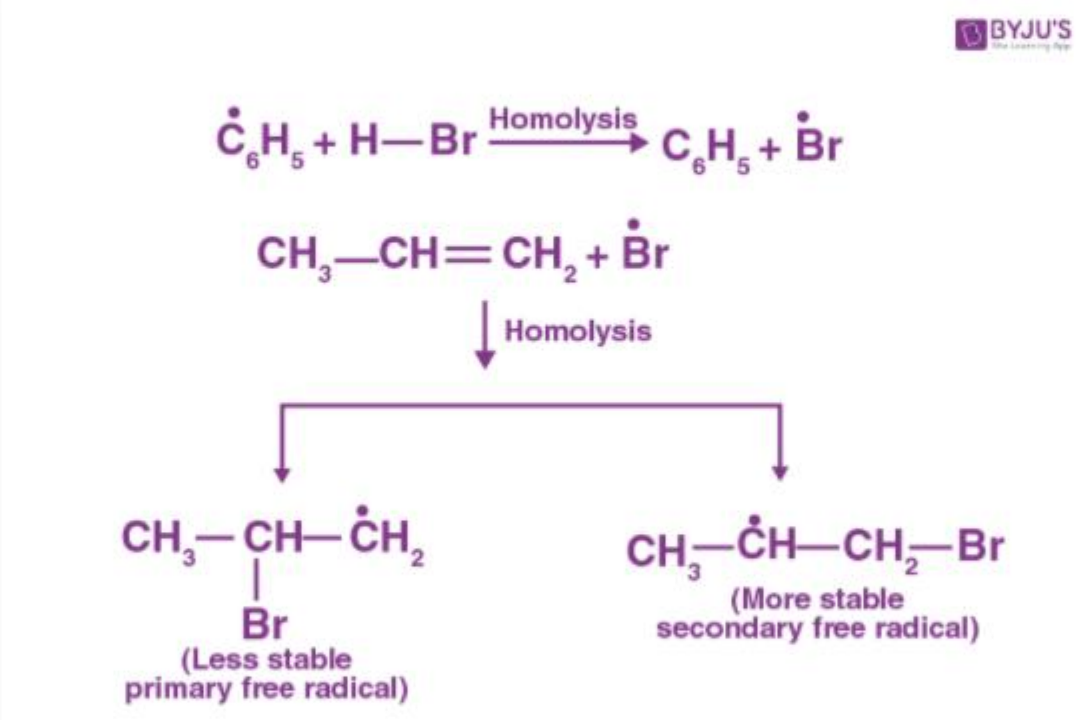


Secondary carbocations are stable in comparison with primary carbocations. The secondary carbocations therefore predominate, as they form at a faster rate than primary carbocations. Thus, Br– attacks the primary carbocation to form 2-bromopropane as the main product in the next step.

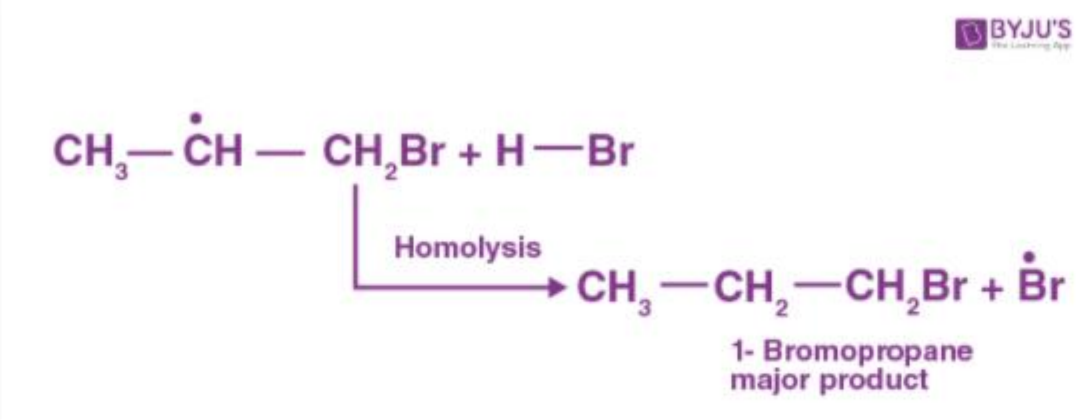
This reaction follows the rule of Markovnikov, in which the negative part of the addendum is attached to the carbon atom with fewer hydrogen atoms than other carbon atoms present in the compound.

While, 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 shown below:





Secondary free radicals are stable in comparison with primary radicals. The secondary radical therefore predominates, for it forms at a faster rate than the primary radical. Therefore 1 – bromopropane is obtained as the main product.



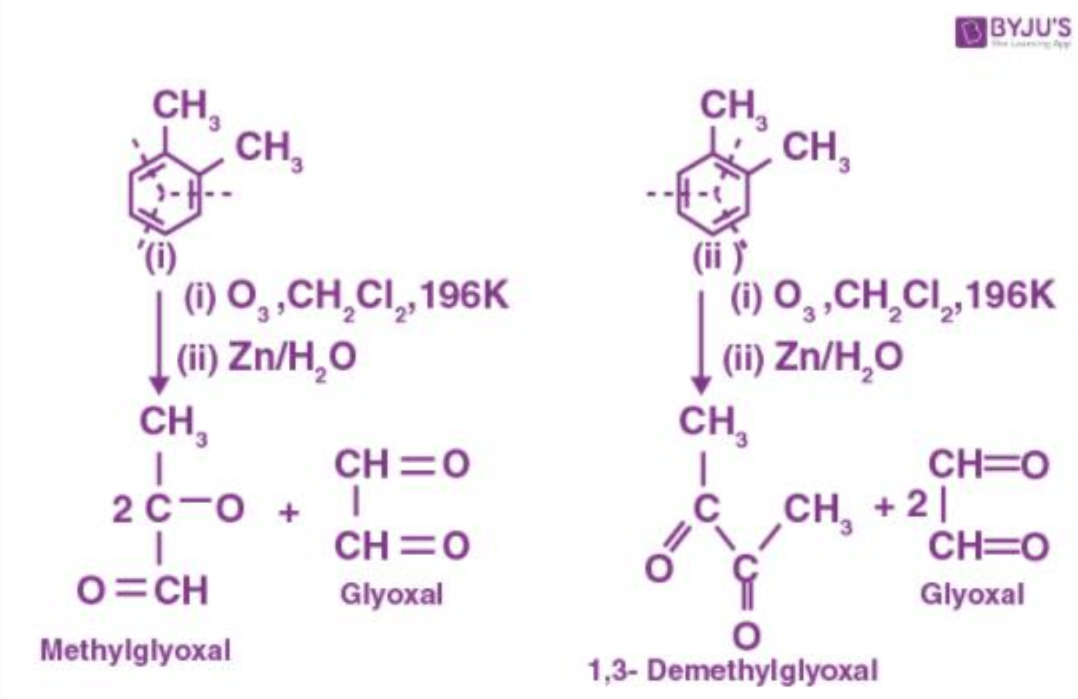
Br acts as an electrophile in the presence of peroxide, as a free radical. Thus, in the presence and absence of peroxide, two different products are obtained on addition of HBr to propene.

Question 13.17:

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

Answer 13.17:

o-xylene has two resonance structures, which are as follows:



All three products are obtained from two Kekule structures of o-xylene, i.e., methyl glyoxal, 1, 2-demethylglyoxal, and glyoxal. As all three products can not be obtained from either of the two structures, this proves that o-xylene is a resonance hybrid of two Kekule (I and II) structures.

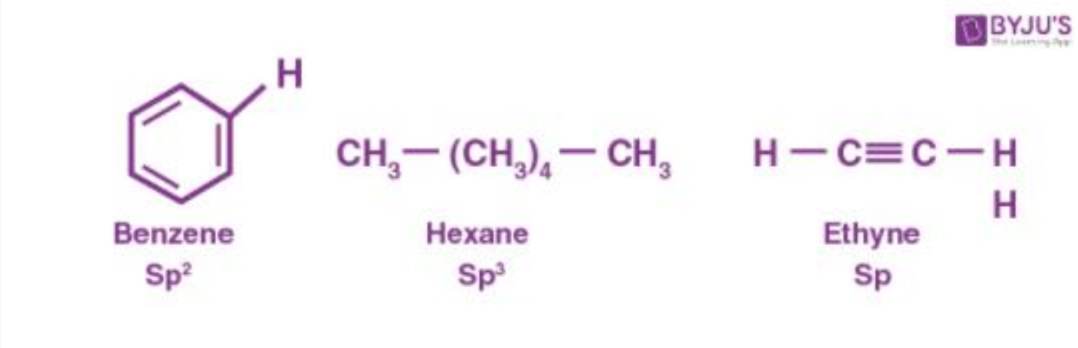
Question 13.18:

Arrange benzene, *n*-hexane and ethyne in increasing order of their acidic behavior. Also, give a reason for this behavior.

Answer 13.18:

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

The hybridization state of carbon in the given compound is:



As the s – character decreases, carbon electronegativity decreases and C – H bond pair electrons lie away from the carbon atom. As a result, H– atom partially positive charge increases, and H+ ions are set free.

The *s*–character decreases in the order:

$sp > sp^2 > sp^3$

Hence, the increasing order of acidic behavior is Hexane < Benzene < Ethyne.

Question 13.19:

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

Answer 13.19:

Benzene is a planar molecule with electrons delocalized under and above the ring plane. Hence, it is a material rich in electrons. As a consequence, electron-deficient species, i.e., electrophiles, are extremely attractive.

Benzene therefore very easily undergoes electrophilic substitution reactions. Nucleophiles, on the other hand, are also species that are rich in electron. Therefore, benzene is repelled as compared to electrophiles. Thus, benzene suffers from difficulty from nucleophilic substitutions.

Question 13.20:

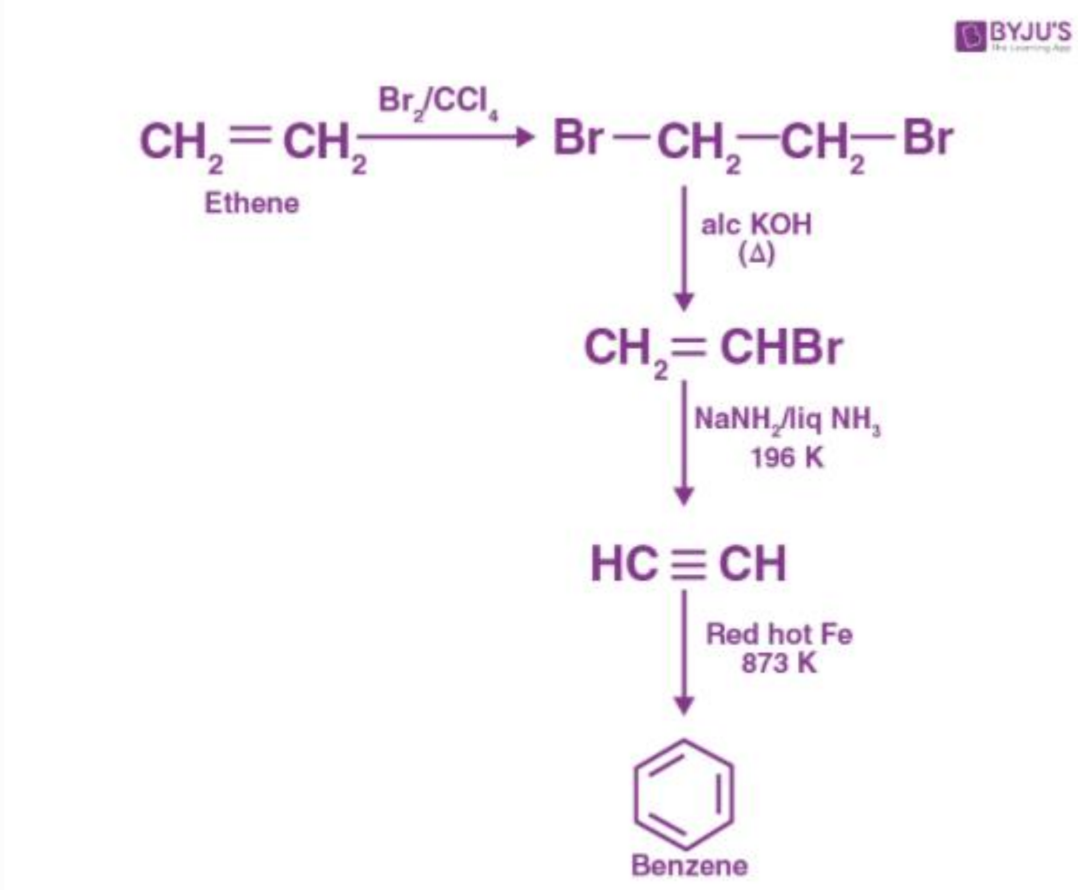
How would you convert the following compounds into benzene?

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

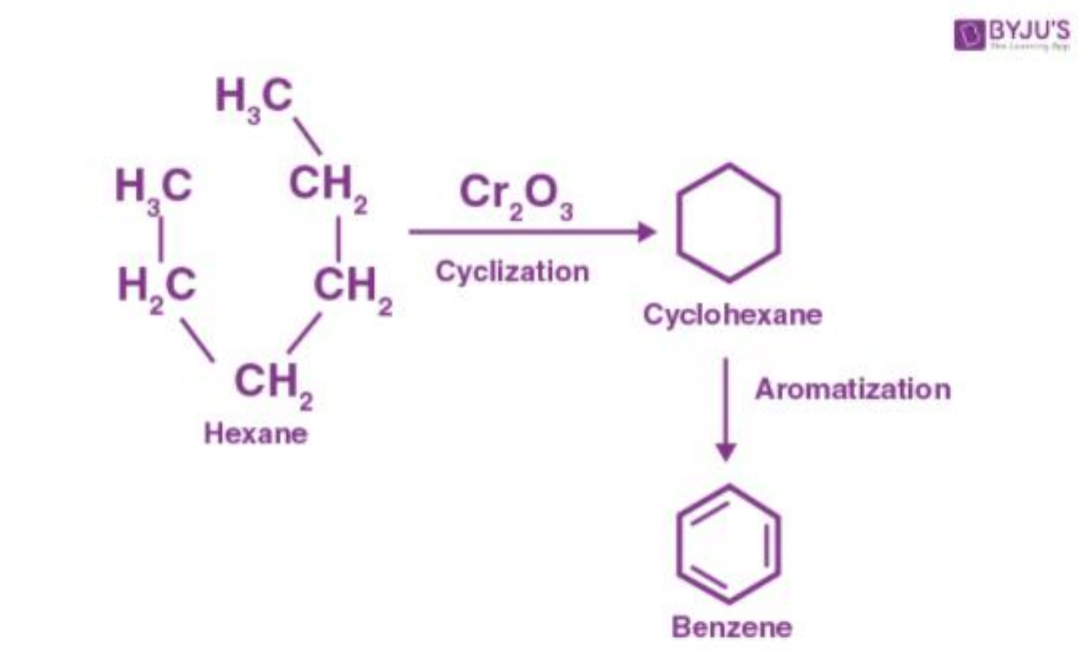
Answer 13.20:

(i)Benzene from Ethyne:

(ii)Benzene from Ethene:



(iii) Hexane to Benzene



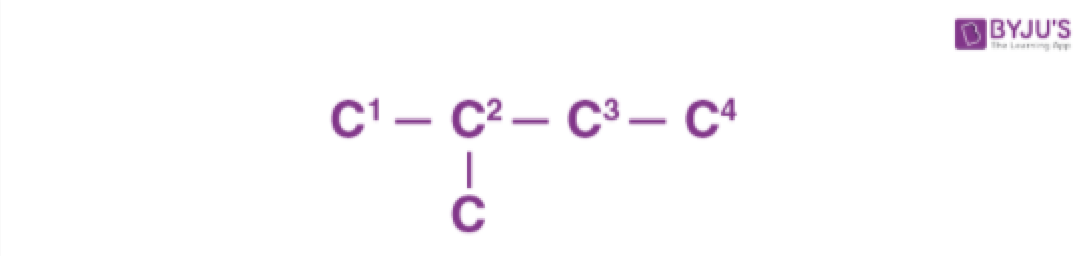
Question 13.21:

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

Answer 13.21:

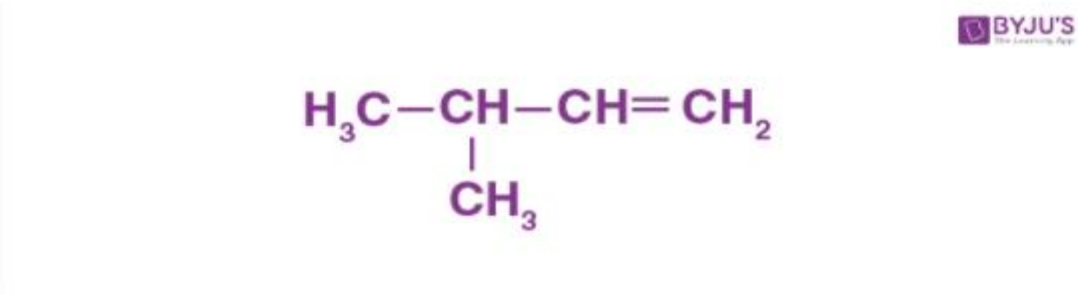
The basic structure of 2-methylbutane is shown below:

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



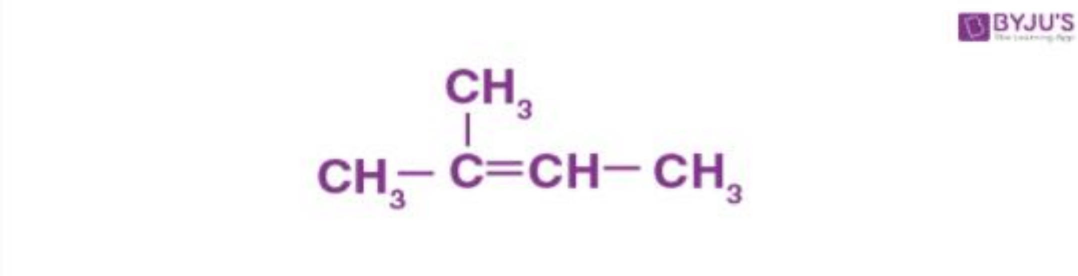
$$C^1-\underset{\overset{|}{C}}{C^2}-C^3-C^4$$

(a)



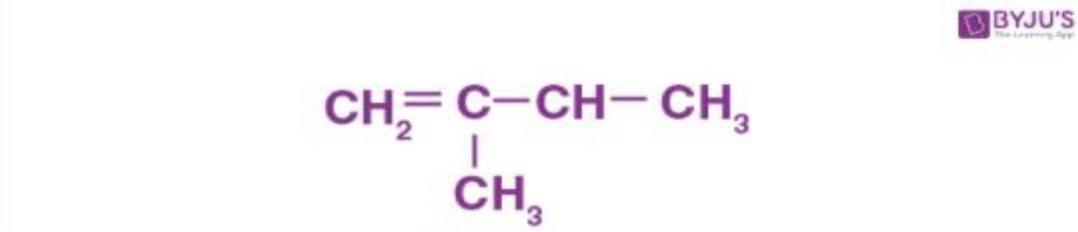
$$H_3C-\underset{\overset{|}{CH_3}}{CH}-CH=CH_2$$

(b)



$$CH_3-\overset{\underset{|}{CH_3}}{C}=CH-CH_3$$

(c)



$$CH_2=\underset{\overset{|}{CH_3}}{C}-CH-CH_3$$

Question 13.22:

Arrange the following set of compounds in order of their increasing relative reactivity with an electrophile, E+

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

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

Answer 13.22:

Electrophiles are reagents that participate in a reaction by accepting a pair of electrons to bind to nucleophiles.

The higher the density of electrons on a benzene ring, the more reactive the compound is to an electrophile, E^+ (Electrophilic reaction).

(a) The electron density of the aromatic ring decreases due to the presence of an electron-withdrawing group (i.e., NO_2 – and Cl –) which deactivates the aromatic ring.

Since, Cl – group is less electron-withdrawing (due to the inductive effect) than NO_2 –group (due to resonance effect), the increasing order of reactivity is as follows:

2, 4 – dinitrochlorobenzene < *p* – nitrochlorobenzene < Chlorobenzene

(b) While NO_2– group is electron-withdrawing, CH_3– is an electron-donating group.

Toluene therefore has the maximum density of electrons, and is most easily attacked by E^+. Since NO_2– is an electron-removing group. Therefore, when the number of NO_2 substitutes is higher, the order is the following.:

p-$O_2N – C_6H_4 – NO_2$ < *p* – $H_3C – C_6H_4 – NO_2$ < Toluene.

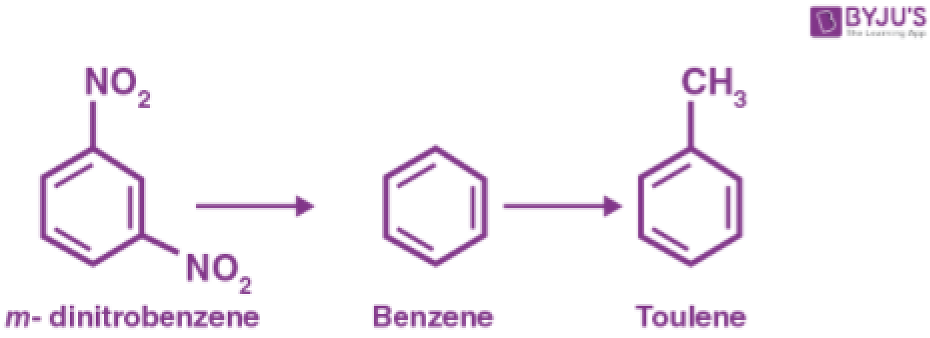
Question 13.23:

Out of benzene, *m*–dinitrobenzene and toluene, state the increasing order of nitration. Justify your answer?

Answer 13.23:

The ease of nitration depends on the presence of electron density on the compound to form nitrates. Nitration reactions are examples of electrophilic substitution reactions where a nitronium ion (NO_2–) attacks an electron-rich species.

Now NO_2– is electron withdrawing and CH_3– group is electron donating. Since, m– Dinitrobenzene will have the least electron density. Hence, it will undergo nitration with difficulty. Therefore, toluene will have the maximum electron density among the three compounds followed by benzene. Hence, the increasing order of nitration is as follows:



Question 13.24:

List the names of some Lewis acid which can be used during ethylation of benzene in a Friedel-Craft alkylation reaction.

Answer 13.24:

The reaction of benzene to the presence of Lewis acids ($AlCl_3$) with an acyl halide or acid anhydride yields acyl benzene (or benzene ring). A Friedel-Craft alkylation reaction is called such a reaction. The reaction occurs in the presence of a Lewis acid.

In the Friedel-Craft alkylation reaction, any Lewis acid such as anhydrous $AlCl_3$, $FeCl_3$, $SnCl_4$, BF_3 etc. may be used during the ethylation of benzene.

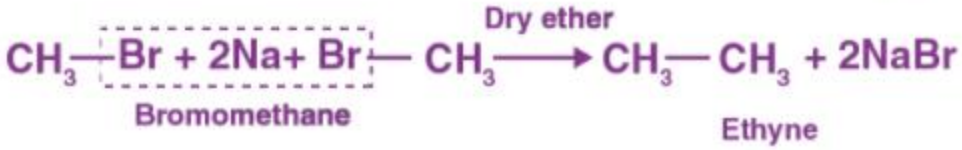
Question 13.25:

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

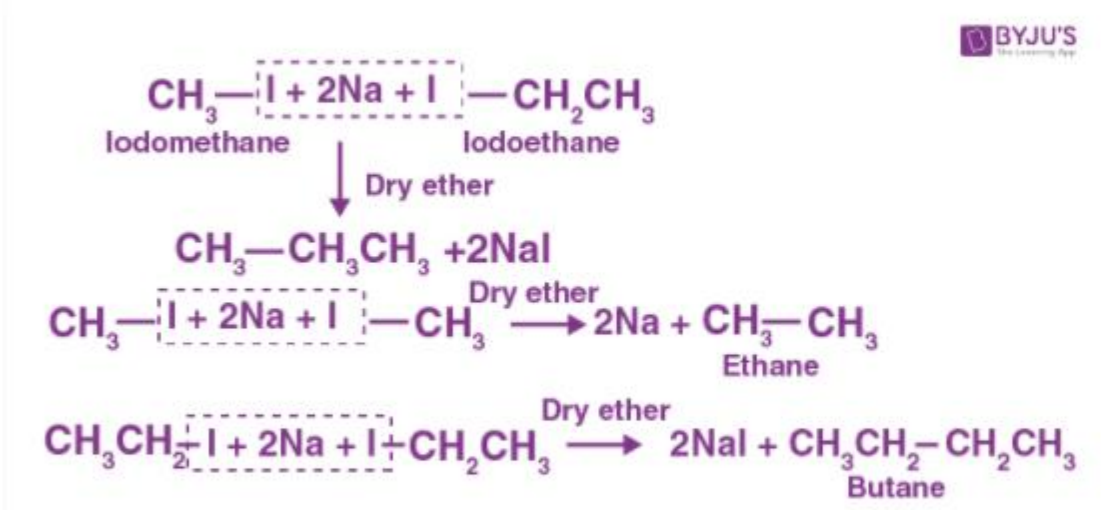
Answer 13.25

For the synthesis of symmetrical alkanes (i.e. alkanes with an even number of carbon atoms), the Wurtz reaction is limited. Two similar alkyl halides are taken as reactants in the reaction, then an alkane is formed which contains double the number of carbon atoms.

Example:



Wurtz reaction can not be used to produce unsymmetric alkanes (i.e. alkanes with an odd number of carbon atoms), because if two dissimilar alkyl halides are used as reactants, a mixture of alkanes is obtained as the items. Since the reaction involves free radical species, there is also a side reaction to creating an alkene.



The boiling points of alkanes (obtained in the mixture) are very close. Hence, it becomes difficult to separate them.