

## Chapter – 13 (Hydrocarbons)

### Exercise Questions:

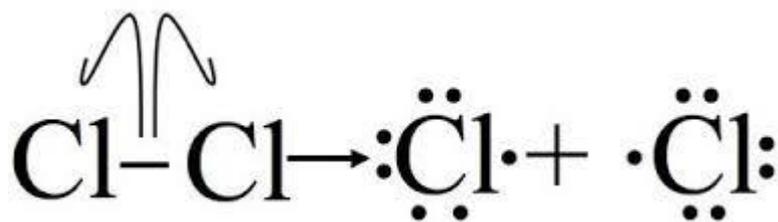
**Question : 1** How do you account for the formation of ethane during chlorination of methane?

Answer:

Chlorination of methane proceeds via a free radical chain mechanism. The whole reaction takes place in the given three steps.

Step 1: Initiation:

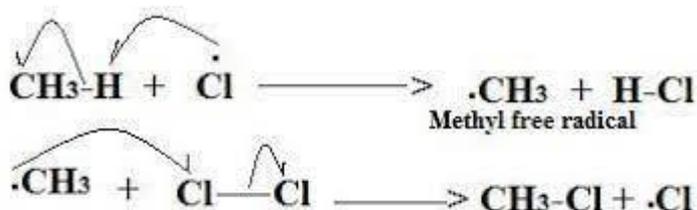
The reaction begins with the homolytic cleavage of Cl- Cl bond as:



Step 2: Propagation:

In the second step, chlorine free radicals attack methane molecules and break down the C- H bond to generate methyl radicals as:

These methyl radicals react with other chlorine free radicals to form methyl chloride along with the liberation of a chlorine free radical.

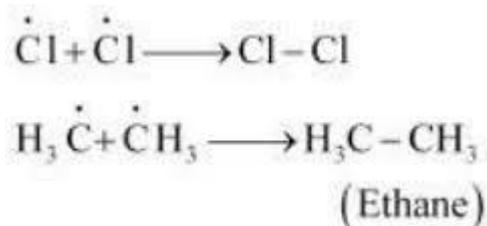


Hence, methyl free radicals and chlorine free radicals set up a chain reaction. While HCl and CH<sub>3</sub>Cl are the major products formed, other higher halogenated compounds are also formed as:



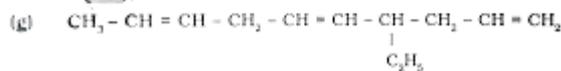
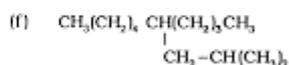
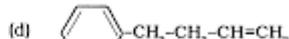
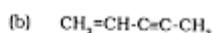
Step 3: Termination:

Formation of ethane is a result of the termination of chain reactions taking place as a result of the consumption of reactants as:



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

**Question: 2 Write the IUPAC names of the following compounds:**



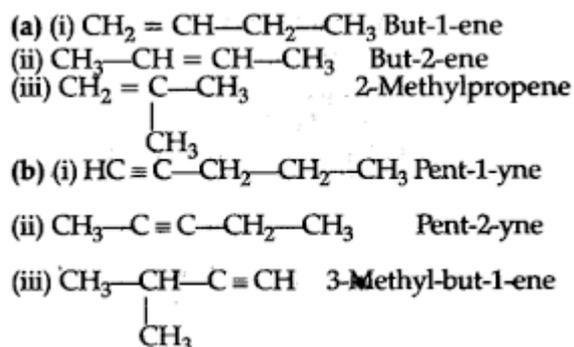
Answer:

- 2-Methylbut-2-ene
- Pen-1-ene-3-yne
- 1,3-Butadiene or Buta-1,3-diene
- 4-Phenylbut-1-ene
- 2-Methylphenol
- 5-(2-Methylpropyl)decane
- 4-Ethyldeca-1,5,8-triene.

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

- $\text{C}_4\text{H}_6$  (one double bond)
- $\text{C}_5\text{H}_8$  (one triple bond)

Answer:



(a)  $\text{C}_4\text{H}_8$  ( one double bond )

Isomers of  $\text{C}_4\text{H}_8$  have one double bond.

- (i)  $\text{CH}_3\text{CH}_2-\text{CH}=\text{CH}_2$  (But-1-ene)
- (ii)  $\text{CH}_3\text{HC}=\text{CCH}_3\text{H}$  ( Cis-but-2-ene)
- (iii)  $\text{CH}_3\text{HC}=\text{CHCH}_3$  ( trans-but-2-ene)
- (iv)  $\text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}_2$  (2-methylprop-1-ene)

(b)  $\text{C}_5\text{H}_8$  ( one triple bond)

Isomers of  $\text{C}_5\text{H}_8$  having one triple bond.

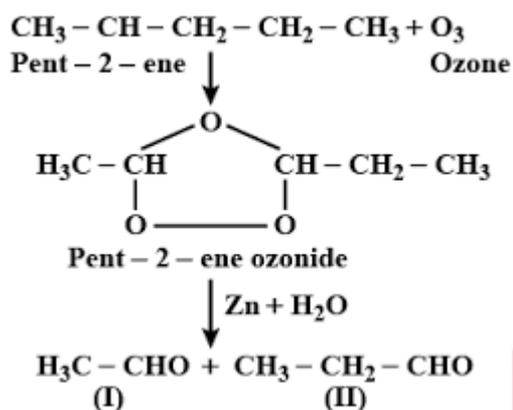
- (i)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$  (pent-1-yne)
- (ii)  $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_3$  (pent-2-yne)
- (iii)  $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{C}\equiv\text{CH}$  ( 3-methylbut-1-yne)

**Question :4** Write the IUPAC names of the product obtained by the ozonolysis of the following compounds :

- I. Pent-2-ene
- II. 3,4-Dimethyl-hept-3-ene
- III. 2-Ethyl-1-ene
- IV. 1-Phenylbut-1-ene

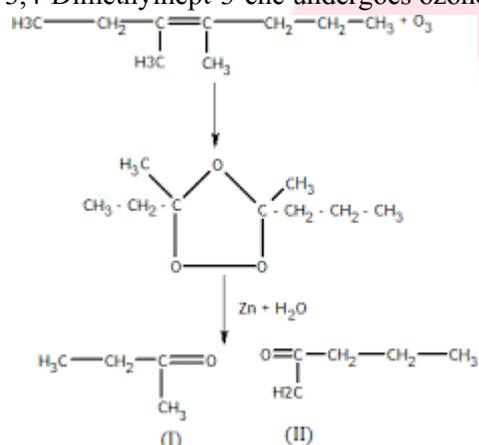
Answer:

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



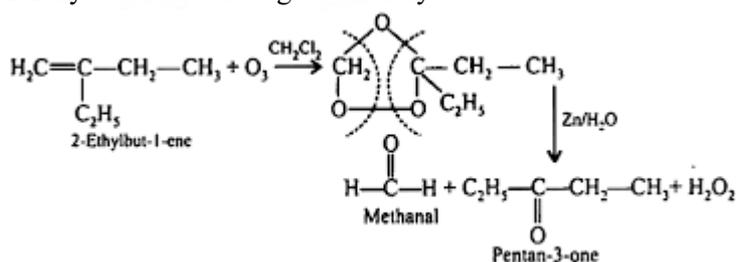
The IUPAC name of product (i) is ethanol and product (ii) is propanal.

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



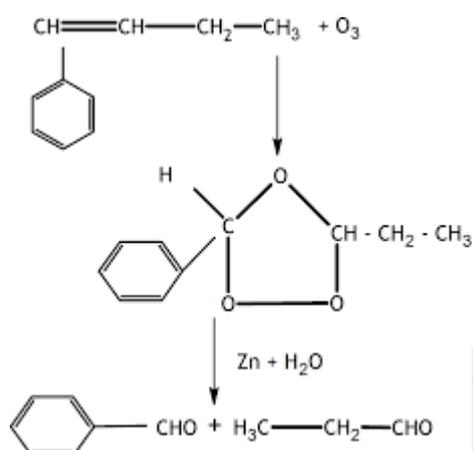
The IUPAC name of product (i) is butan-2-one and product (ii) is pentan-2-one.

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



The IUPAC name of product (i) is pentan-3-one and product (ii) is methanol.

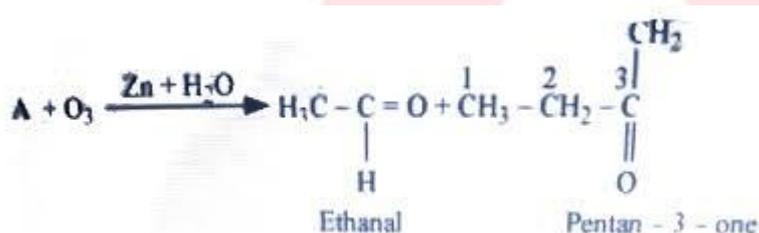
iv.) 1-Phenylbut-1-ene undergoes ozonolysis as:



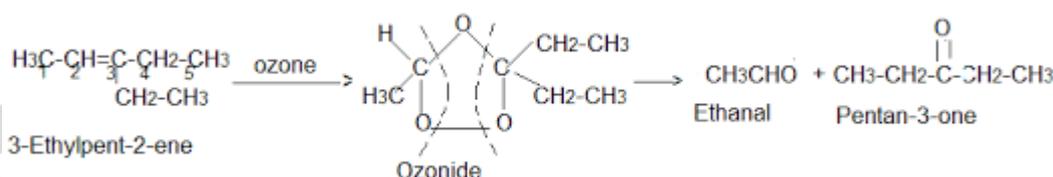
The IUPAC name of product (i) is benzaldehyde and product (ii) is propanal.

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

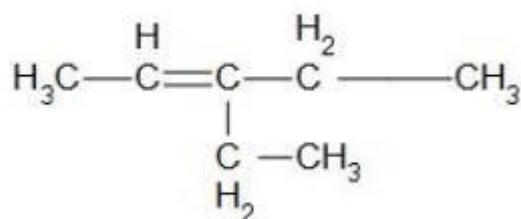
Answer:



During ozonolysis, an ozonide having a cyclic structure is formed as an intermediate which undergoes cleavage to give the final products. Ethanal and pentan-3-one are obtained from the intermediate ozonide. Hence, the expected structure of the ozonide is:

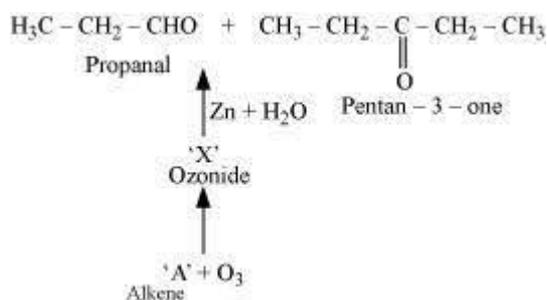


This ozonide is formed as an addition of ozone to 'A'. The desired structure of 'A' can be obtained by the removal of ozone from the ozonide. Hence, the structural formula of 'A' is:

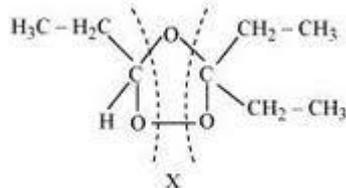


The IUPAC name of 'A' is 3-Ethylpent-2-ene.

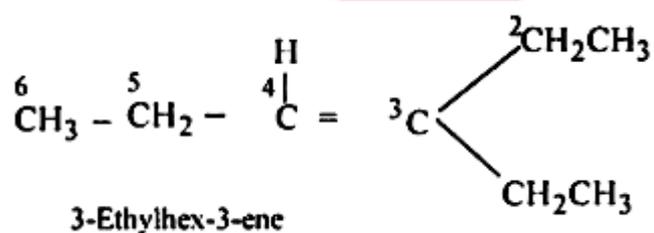




The products are obtained on the cleavage of ozonide 'X'. Hence, 'X' contains both products in the cyclic form. The possible structure of ozonide can be represented as:



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

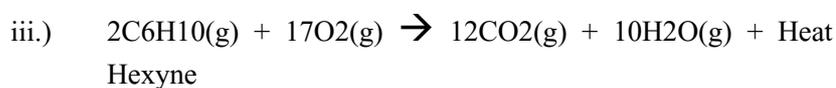
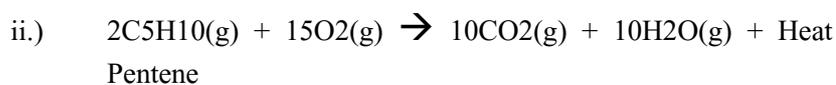
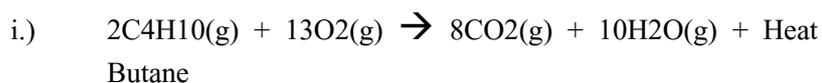


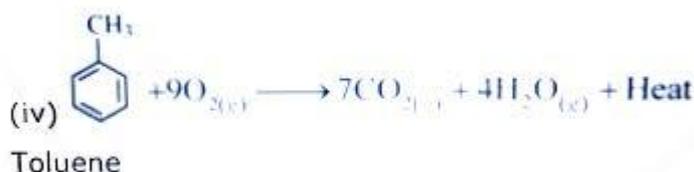
**Question :8 Write the chemical equations for combustion reaction of the following hydrocarbons :**

- I. Butane
- II. Pentene
- III. Hexyne
- IV. Toluene

Answer:

Combustion can be defined as a reaction of a compound with oxygen.





iv.)

**Question :9 Draw the cis and trans structures of hex-2-ene. Which isomer will have higher boiling point and why?**

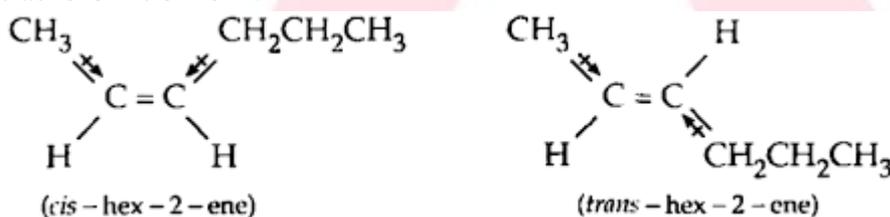
Answer:

Complete structure formula of Hex-2-ene is  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH=CH-CH}_3$ , now the structure of cis - and trans- isomers of hex-2-ene is shown in pic.

Cis - form is more polar form than trans form {due to this cis -form has higher dipole moment than trans - form .

We know, the boiling point depends upon dipole - dipole interactions.

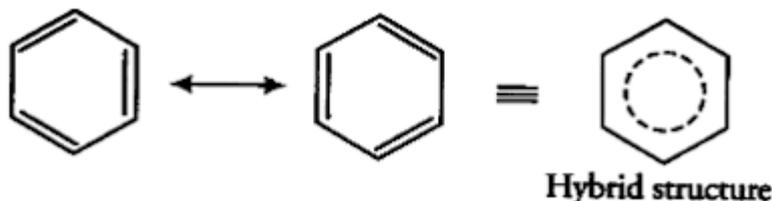
The boiling point of cis - isomer is greater than that of trans - isomers, due to greater dipole- dipole interactions in cis - form.



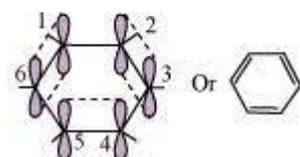
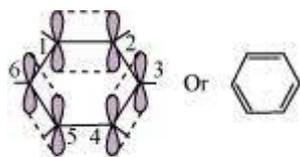
**Question :10 Why is benzene extra ordinarily stable though it contains three double bonds?**

Answer:

Benzene is a hybrid of resonating structures given as:



All six carbon atoms in benzene are  $\text{sp}^2$  hybridized. The two  $\text{sp}^2$  hybrid orbitals of each carbon atom overlap with the  $\text{sp}^2$  hybrid orbitals of adjacent carbon atoms to form six sigma bonds in the hexagonal plane. The remaining  $\text{sp}^2$  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  $\pi$  bonds by the lateral overlap of . C1 - C2, C3- C4, C5 - C6, or C2 - C3, C4-C5, C6-C1.



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

**Question :11 What are the necessary conditions for any system to be aromatic?**

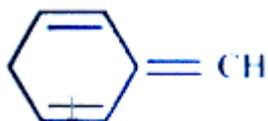
Answer :

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

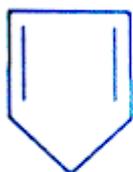
- I. It should have a planar structure.
- II. It should be cyclic.
- III. The electrons of the compound are completely delocalized in the ring.
- IV. The total number of electrons present in the ring should be equal to  $(4n + 2) L$ , where,  $n = 0, 1, 2, \dots$  etc. This is known as Huckel's rule.

**Question : 12 Explain why the following systems are not aromatic?**

(i)



(ii)



(iii)



Answer:

(i) For the given compound, the number of  $\pi$ -electrons is six. But only four  $\pi$ -electrons are present within the ring. Also there is no conjugation of  $\pi$ -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  $\pi$ -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 ( $n = 0, 1, 2, \dots$ ), which is not true for the given compound. Hence, it is not aromatic in nature.

(iii) For the given compound, the number of  $\pi$ -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 ( $n = 0, 1, 2, \dots$ ). Since the value of  $n$  is not an integer, the given compound is not aromatic in nature.

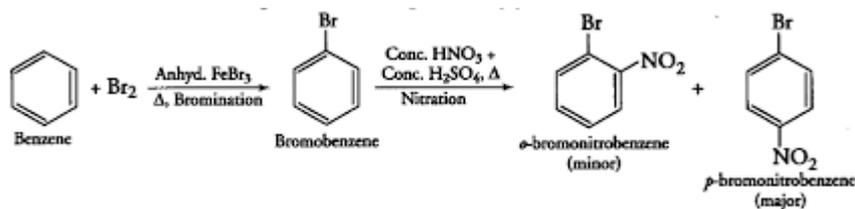
**Question :13 How will you convert benzene into**

- I. P-nitrobromobenzene
- II. M-nitrochlorobenzene

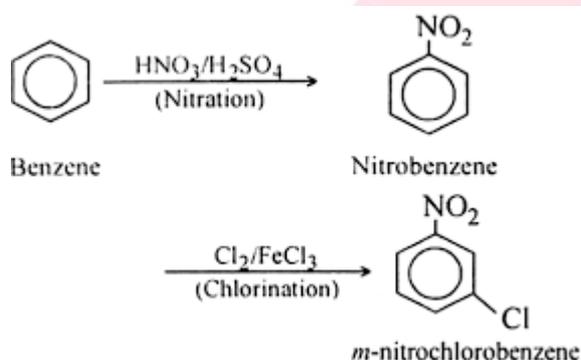
### III. P-nitrotoluene

### IV. Acetophenone

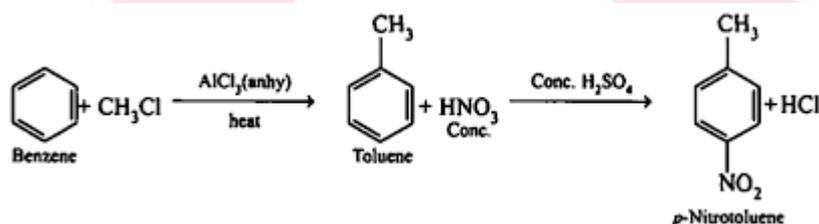
Answer:



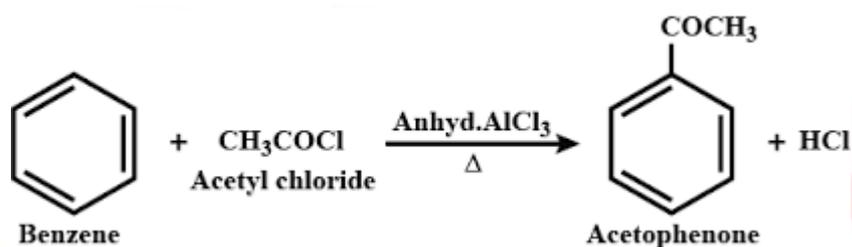
i.)



ii.)



iii.)



iv.)

**Question : 14** In the alkane  $\text{H}_3\text{-CH}_2\text{-C}(\text{CH}_3)_2\text{-CH}_2\text{-CH}(\text{CH}_3)_2$ , identify primary, secondary, tertiary carbon atoms and give the number of H atom bonded to each one of these.

Answer:

Primary carbon atoms are those which are bonded to only one carbon atom or none. I. E., they have only one carbon atom as their neighbour or none in case of methane. The given structure has five primary carbon atoms and fifteen hydrogen atoms attached to it.

Secondary carbon atoms are those which are bonded to two carbon atoms example they have two carbon atoms as their neighbours. The given structure has two secondary carbon atoms and four hydrogen atoms attached to it.

Tertiary carbon atoms are those which are bonded to three carbon atoms example they have three carbon atoms as their neighbours. The given structure has one tertiary carbon atom and only one hydrogen atom is attached to it.

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

Answer :

Alkanes experience inter – molecular Van der Waals forces. The stronger the force, the greater will be the boiling point of the alkane.

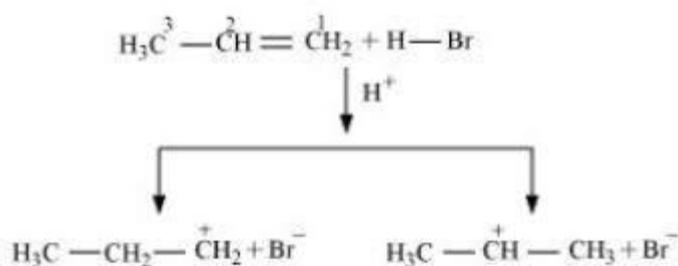
As branching increases the surface area of the molecule decreases which results in a smaller area of contact. As a result, the Van der Waals force also decreases which can be overcome at a relatively lower temperature. Hence, the boiling point of an alkane chain decreases with an increase in branching.

**Question : 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.**

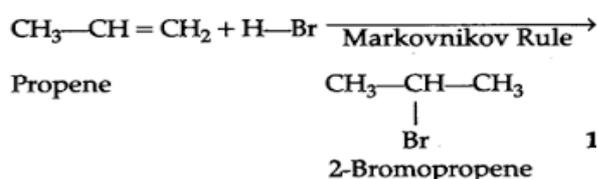
Answer:

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

Hydrogen bromide provides an electrophile, H<sup>+</sup>. This electrophile attacks the double bond to form 1<sup>o</sup> and 2<sup>o</sup> carbocations as shown:

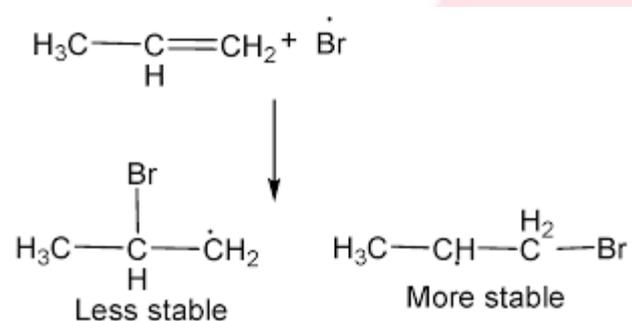
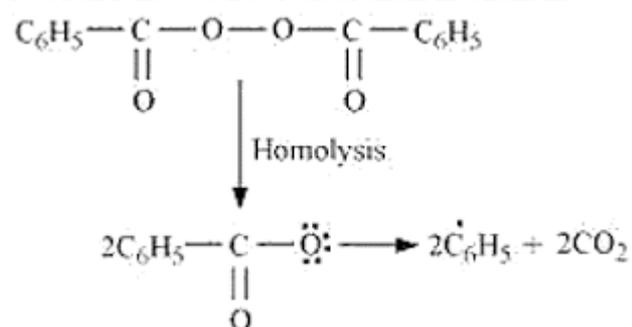


Secondary carbocations are more stable than primary carbocations. Hence, the former predominates since it will form at a faster rate. Thus, in the next step, Br<sup>-</sup> attacks the carbocation to form 2-bromopropane as the major product.

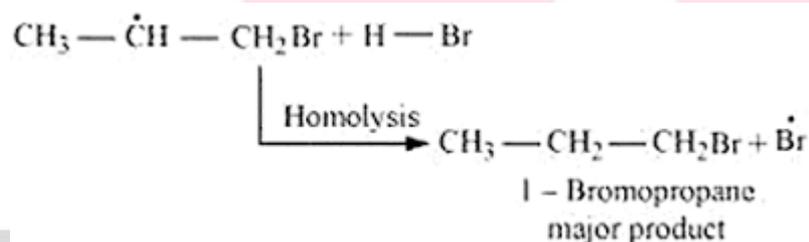


This reaction follows Markovnikov's rule where the negative part of the addendum is attached to the carbon atom having a lesser number of hydrogen atoms.

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.

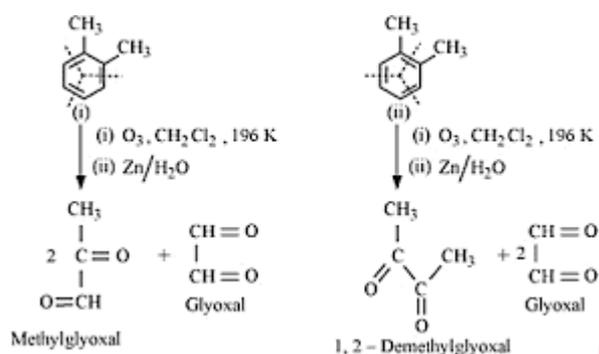


In the presence of peroxide, Br free radical acts as an electrophile. Hence, two different products are obtained on addition of HBr to propene in the absence and presence of peroxide.

**Question :17 Write down the products of ozonolysis of 1,2-dimethylbenzene. How does the result support Kekule structure for benzene?**

Answer:

O-xylene has two resonance structures:



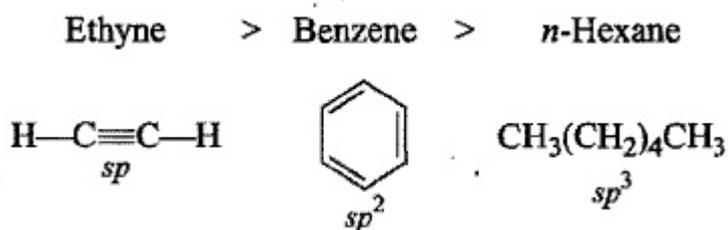
All three products, i.e., methyl glyoxal, 1, 2-demethylglyoxal, and glyoxal are obtained from two Kekule structures. Since all three products cannot be obtained from any one of the two structures, this proves that o-xylene is a resonance hybrid of two Kekule structures (I and II).

**Question :18 Arrange benzene, n – hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behavior.**

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:



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<sup>+</sup> ions are set free.

The s-character increases in the order:



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

**Question :19 Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?**

Answer :

Benzene is a planar molecule having delocalized electrons above and below the plane of ring. Hence, it is electron -rich. As a result, it is highly attractive to electron deficient species example electrophiles.

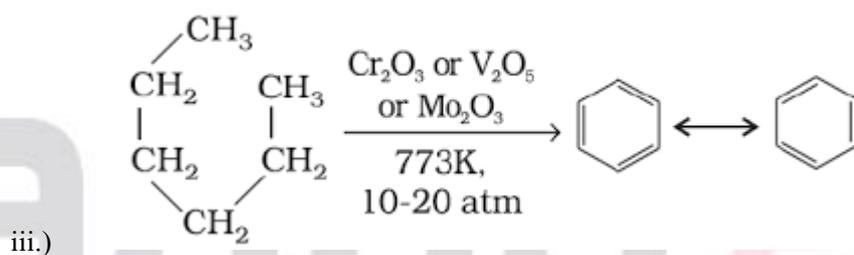
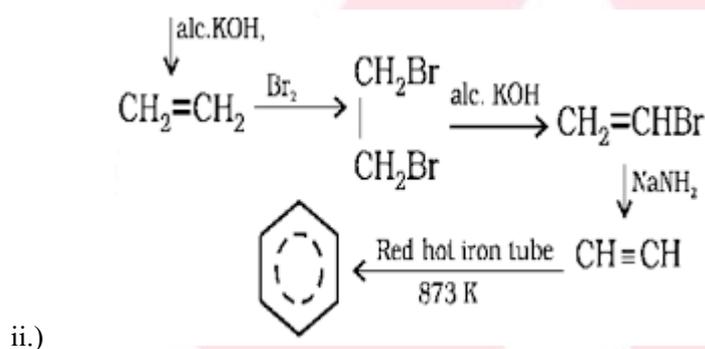
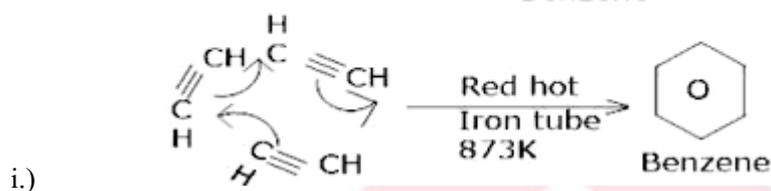
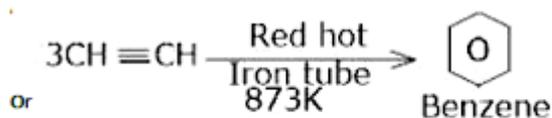
Therefore, it undergoes electrophilic substitution reactions very easily. Nucleophilic are electron – rich.

Hence, benzene undergoes nucleophilic substitutions with difficulty.

**Question : 20** How would you convert the following compounds into benzene?

- I. Ethyne
- II. Ethene
- III. Hexane

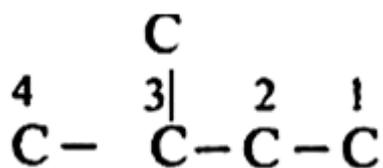
Answer:



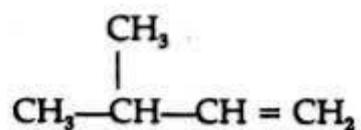
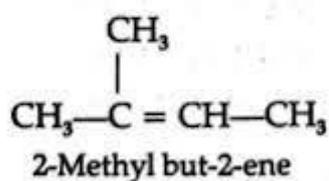
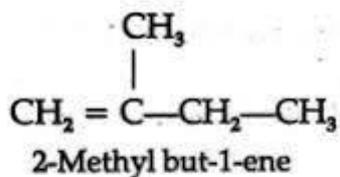
**Question :21** Write structures of all alkenes which on hydrogenation give 2-methylbutane.

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:



**Question :22** Arrange the following set of compounds in order of their decreasing relative with an electronics, E+

- Chlorobenzene, 2,4-dinitrochlorobenzene, p-nitrochlorobenzene
- Toluene, p-H<sub>3</sub>C-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>, p-O<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-No<sub>2</sub>.

Answer:

Electrophiles are reagents that participate in a reaction by accepting an electron pair in order to bond to nucleophiles.

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

(a) The presence of an electron withdrawing group (i.e., NO<sub>2</sub>- and Cl-) deactivates the aromatic ring by decreasing the electron density.

Since NO<sub>2</sub>- 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<sub>3</sub>- is an electron donating group, NO<sub>2</sub>- group is electron withdrawing. Hence, toluene will have the maximum electron density and is most easily attacked by E<sup>+</sup>.

NO<sub>2</sub>- is an electron withdrawing group. Hence, when the number of NO<sub>2</sub>- substituents is greater, the order is as follows:

Toluene > p-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>, p-O<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>

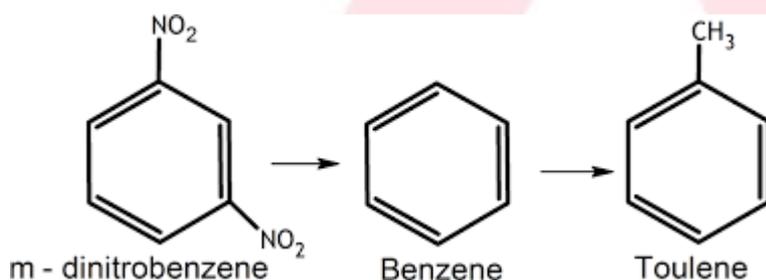
**Question :23 Out of benzene, m-dinitrobenzene and toluene which will undergo nitration most easily and why?**

Answer:

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 an electron-rich species is attacked by a nitronium ion (NO<sub>2</sub><sup>+</sup>).

Now, CH<sub>3</sub>- group is electron donating and NO<sub>2</sub>- is electron withdrawing. Therefore, toluene will have the maximum electron density among the three compounds followed by benzene. On the other hand, m-Dinitrobenzene will have the least electron density. Hence, it will undergo nitration with difficulty.

Hence, the increasing order of nitration is as follows:



**Question :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 Friedel-Craft alkylation reaction. This reaction takes place in the presence of a Lewis acid.

Any Lewis acid like anhydrous FeCl<sub>3</sub>, SnCl<sub>4</sub>, BF<sub>3</sub>, etc. can be used during the regulation of benzene.

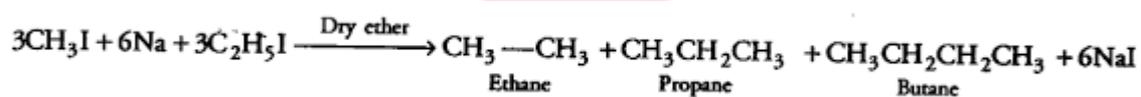
**Question :25 Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example.**

Answer:

In Wurtz reaction, when preferred for the preparation of alkanes containing odd number of carbon atoms, then it means two different alkyl halides are taken and two different alkyl halides can react in three different ways. Therefore a mixture of alkanes is produced.

That's why Wurtz reaction doesn't suitable for the preparation of alkanes containing odd number of carbon atoms.

See the example shown in figure. here two different alkyl halides,  $\text{CH}_3\text{I}$  and  $\text{C}_2\text{H}_5\text{I}$  are taken for the preparation of the alkanes. But we observed, alkanes are the mixture of Ethane, propane and butane.



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