

NCERT SOLUTIONS

CLASS-XI CHEMISTRY

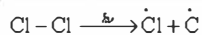
CHAPTER-13

HYDROCARBONES

Question 13.1: How do you explain for the generation of ethane through chlorination of methane?

Answer 13.1: The process of chlorination of methane works via a free radical chain mechanism. There are steps for this whole reaction.

Step 1: Initiation:

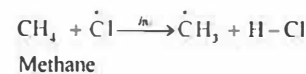


The result begins with the hemolytic cleavage of Cl – Cl bond as

Chlorine free radicals

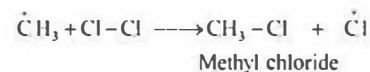
Step 2: Propagation:

In the next step, methane molecules are attacked by chlorine free radicals and it collapses the C- H bond to form methyl radicals as :



Methane

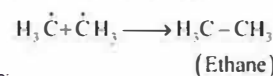
Methyl chloride next to the liberation of a chlorine free radical is formed when these methyl radicals react with the other chlorine free radicals.



Methyl chloride



Step 3: Termination:



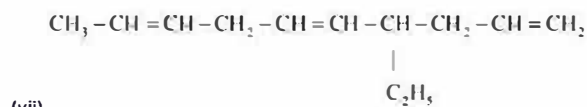
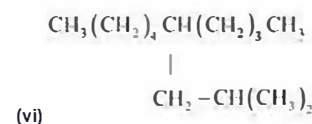
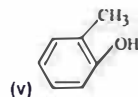
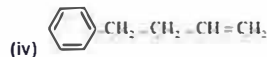
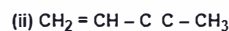
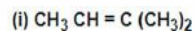
(Ethane)

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

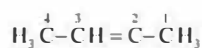
Hence, by this process, ethane is obtained as a by-product of chlorination of methane.

Question 13.2:

For the following compounds, note down the IUPAC names :

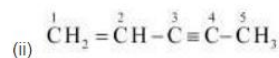


Answer 13.2:





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

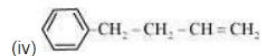
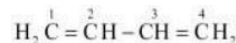


Pen-1-ene-3-yne is the required IUPAC name

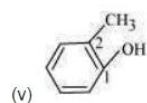
(iii)



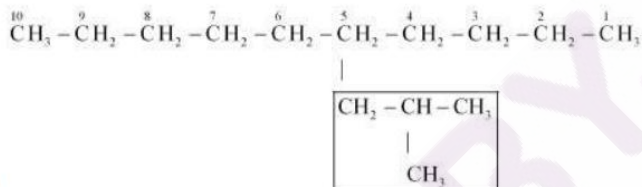
1, 3-Butadiene or Buta-1,3-diene is the required IUPAC name



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

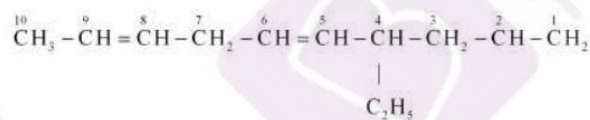


2-Methyl phenol is the required IUPAC name



(vi)

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



(vii)

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

Question 13.3:

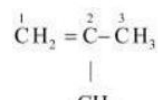
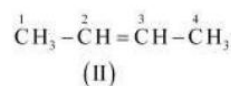
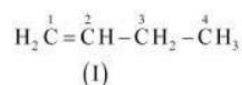
Write IUPAC names and structural formulas for all possible isomers having the number of double or triple bond as indicated for the following compounds:

(a) C_4H_8 (one double bond)

(b) C_5H_8 (one triple bond)

Answer 13.3:

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





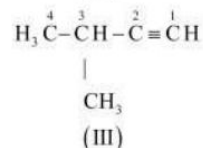
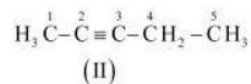
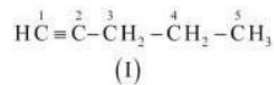
The IUPAC name of

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-yne.

Question 13.4:

For the following compounds, note down the IUPAC names of product formed by the ozonolysis of the

(i) Pent-2-ene

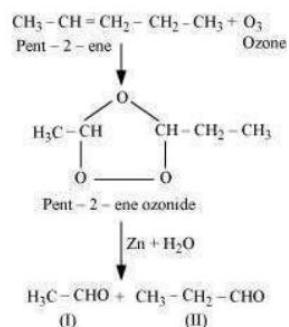
(ii) 3, 4 – Dimethyl-hept-3-ene

(iii) 2-Ethylbut-1-ene

(iv) 1 – Phenylbut-1-ene

Answer 13.4:

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

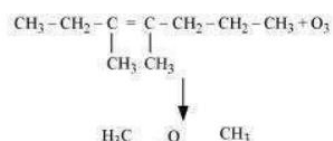


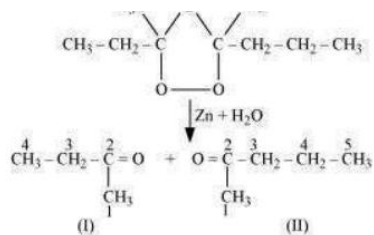
The subsequent IUPAC names of the products are :

Product (I) ethanal, and

Product (II) propanal.

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



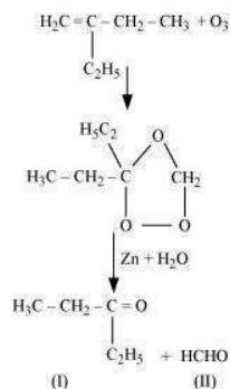


The subsequent IUPAC names of the products are :

Product (I) butan-2-one, and

Product (II) Pentan-2-one

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

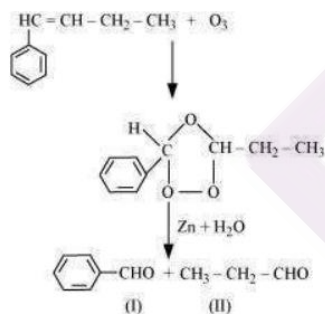


The subsequent IUPAC names of the products are:

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 :

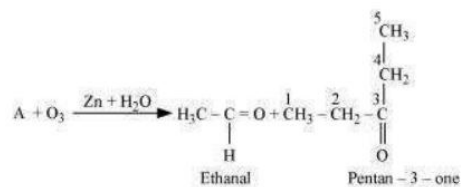
Product (I) benzaldehyde, and

Product (II) propanal

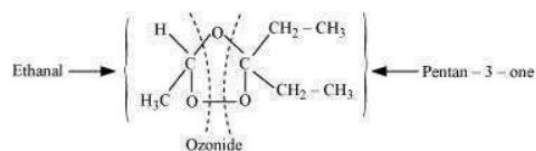
Question 13.5:

Pentan-3-one and ethanal is a mixture formed by ozonolysis of an alkene 'A'. Mention the IUPAC name and the name of 'A'.

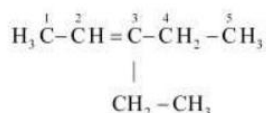
Answer 13.5:



An ozonide is produced as an intermediate which has a cyclical structure during ozonolysis; it undergoes cleavage to provide the concluding products. Ethanal and pentan-3-one are obtained from the intermediate ozonide. So, the possible structure of the ozonide will be:



On addition of ozone to 'A' this ozonide is produced as a transitional which forms final products on undergoing cleavage. The preferred arrangement of 'A' can be obtained by the elimination of ozone from the ozonide. Hence, the structural formula of 'A' is:



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

Question 13.6:

Note down the IUPAC name of 'A' when an alkene 'A' contains one C – C π bond, three C-C bonds, and eight C – H σ , two moles of an aldehyde of molar mass 44 u is obtained on ozonolysis of alkene 'A'.

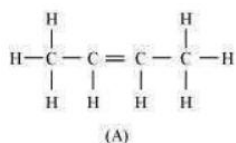
Answer 13.6:

From the given information, when 'A' undergoes ozonolysis, it gives two moles of an aldehyde of molar mass 44 u. The formation of the two moles of an aldehyde indicates that there is the presence of identical structural units on both sides of the C-C π bond. Hence, the structure of 'A' can be represented as shown below:

We know, XC = CX

Since there are eight C-H σ bonds, hence, there are 8 hydrogen atoms in 'A'. Also, there are three C-C bonds, so, there are four carbon atoms present in the structure of 'A'.

Combining all these inferences, the structure of 'A' can be represented as shown below:

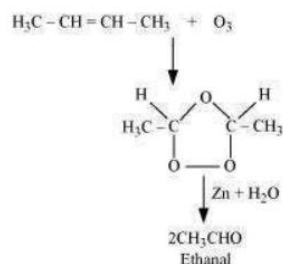


Since, 'A' has 3 C-C bonds, 8 C-H σ bonds, and one C-C π bond.

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

After Ozonolysis of 'A' takes place,

The final product is ethanal with molecular mass = 44 u



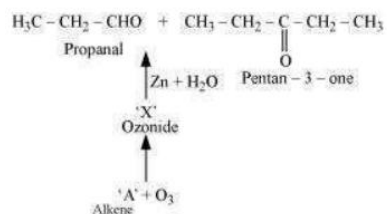
Question 13.7:

The products formed on ozonolysis of alkene are pentan-3-one and propanal? Write the structural formula of the alkene?

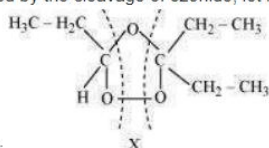
Answer 13.7:

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

Suppose the given alkene be 'A'. Undergoing the reverse of the ozonolysis reaction, we get:

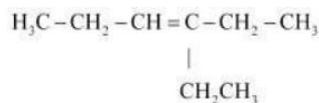


The products that are obtained by the cleavage of ozonide, let it be 'X'. Since 'X' contains both products in the cyclic form, so the possible structure of ozonide can be



represented as shown below:

Since 'X' is an addition product of alkene 'A' with ozone. Therefore, the possible structure of the given alkene 'A' will be:



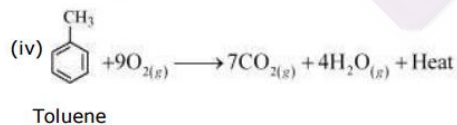
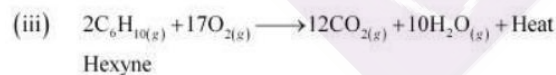
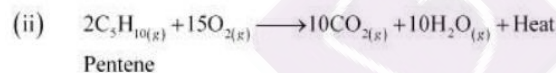
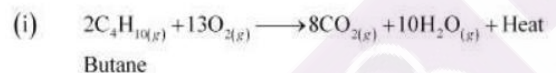
Question 13.8:

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

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

Answer 13.8:

Combustion reactions can be defined as a reaction of a compound in the presence of oxygen or with the oxygen.

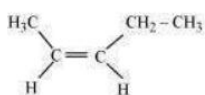


Question 13.9:

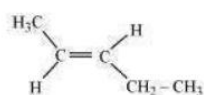
Sketch the trans and cis structures of hex-2-ene. Also, the state which isomer will have higher b.p. and why?

Answer 13.9:

Hex-2-ene is represented as shown below: $\text{H}_3\text{C}-\text{HC}=\text{CH}-\text{CH}_2-\text{CH}_3$



Cis-isomer



Trans-isomer

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

The dipole moment of a cis-compound is equal to the sum of the dipole moments of the C-CH₃ bond and the C-CH₂CH₃ bonds both acting in the same direction.

On the other hand, the dipole moment of a trans-compound is the resultant of the dipole moments of C-CH₃ bond and C-CH₂CH₃ bonds both acting in opposite directions.

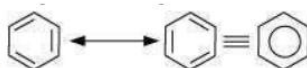
Since cis-isomer is more polar than trans-isomer. So, higher the polarity, the greater is the intermolecular dipole-dipole interaction and more heat are required to break the bonds. Hence, the boiling will be higher.

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

Question 13.10:

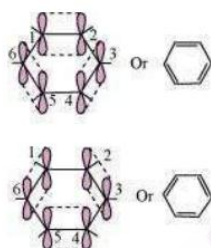
Although benzene contains three double bonds state why it is extraordinarily stable?

Answer 13.10:



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

In benzene all the six carbon atoms are sp^2 hybridized. In benzene the two sp^2 hybrid orbital of each carbon atom overlap with the sp^2 hybrid orbital of its adjacent carbon atoms, so as to form a six sigma bonds in the hexagonal plane. The remaining sp^2 hybrid orbital on each carbon atom overlaps with the s-orbital of the hydrogen atom to form six sigma C-H bonds. Now, the remaining un-hybridized p-orbital of carbon atoms will have the possibility of forming three C-C π bonds by the lateral overlap of $C_1-C_2, C_3-C_4, C_5-C_6$, or $C_2-C_3, C_4-C_5, C_6-C_1$.



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

Question 13.11:

Mention for any system to be aromatic what are the essential conditions?

Answer 13.11:

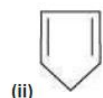
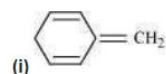
The essential conditions for any system to be aromatic are as follows:

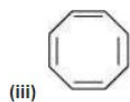
- Firstly, the arrangement or the structure of the compound should be planar.
- In the ring of a compound, the n - electrons are entirely delocalized
- In the ring of a compound, the sum of n - electrons must be equal to $(4n + 2)$,

Where $n = 0, 1, 2, \dots$ and so on. This rule is called Huckel's rule.

Question 13.12:

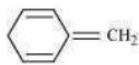
Check whether the given systems below are aromatic or not. Explain with clear reason.





Answer 13.12:

(i)



The total number of π – electrons in the given compound is 6.

From Huckel's rule,

$$4n + 2 = 6$$

$$4n = 4$$

$$n = 1$$

In Huckel's rule, the ring of a compound having the π – electrons should be equal to $= 0, 1, 2, \dots$ and so on i.e., n must be an integer. While the n of the given compound is an integer and the given compound is aromatic in nature.

(ii)



The total number of π – electrons in the given compound is 4.

From Huckel's rule,

$$4n + 2 = 4$$

$$4n = 2$$

$$n = 1 / 2$$

In Huckel's rule, the ring of a compound having the π – electrons should be equal to $= 0, 1, 2, \dots$ and so on i.e., n must be an integer. While the n of the given compound is not an integer and the given compound is not aromatic in nature.

(iii)



The total number of π – electrons in the given compound is 8.

From Huckel's rule,

$$4n + 2 = 8$$

$$4n = 6$$

$$n = 3 / 2$$

In Huckel's rule, the ring of a compound having the π – electrons should be equal to $= 0, 1, 2, \dots$ and so on i.e., n must be an integer. While the n of the given compound is not an integer and the given compound is not aromatic in nature.

Question 13.13:

Show how benzene is converted into

(i) **p – nitrobromobenzene**

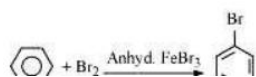
(ii) **m-nitrochlorobenzene**

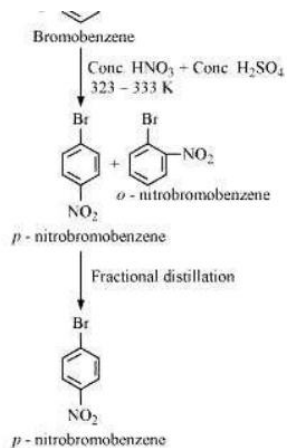
(iii) **p -nitrotoluene**

(iv) **acetophenone**

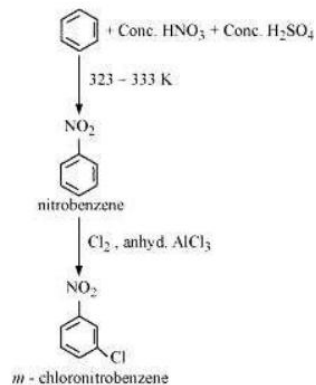
Answer 13.13:

(i) Benzene converted to p – nitrobromobenzene

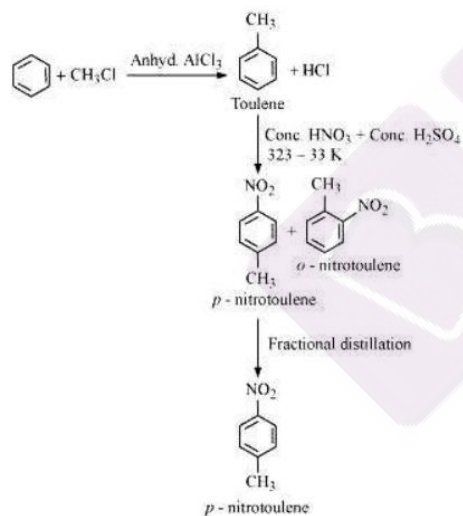




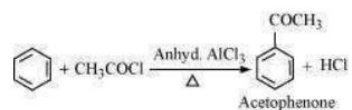
(ii) Benzene converted to *m*-nitrochlorobenzene



(iii) Benzene converted to *p*-nitrotoluene



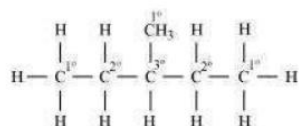
(iv) Benzene converted to acetophenone



Question 13.14:

Classify the alkane $\text{H}_3\text{C} - \text{CH}_2 - \text{C}(\text{CH}_3)_2 - \text{CH}_2 - \text{CH}(\text{CH}_3)_2$, on the basis of primary, secondary and tertiary carbon atoms and find the number of H atoms bonded to each carbon atom

Answer 13.14:



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

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

Tertiary carbon atoms (3°): Carbon atoms bonded to a single carbon atom is called tertiary carbon atom. The arrangement given has one 3° carbon atoms and single H atoms corresponding to it.

Question 13.15:

How the boiling point of an alkane gets affected by branching of an alkane chain?

Answer 13.15:

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

As branching of the molecule increases, the surface area decreases which results in a small area of contact. As a result, the Van-der Waals force (or the intermolecular force) also decreases. At a relatively lower temperature, these forces can be overcome very easily. Hence, the boiling point of an alkane chain decreases with an increase in branching.

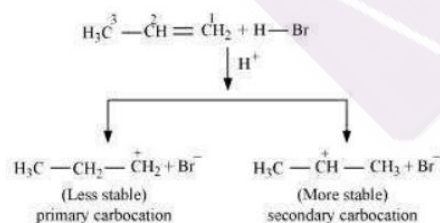
Question 13.16:

In the presence of benzoyl peroxide, propene yields 1-bromopropane, while in addition of HBr to propene, it yields 2-bromopropane. Explain through the mechanism.

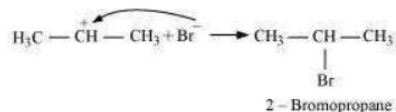
Answer 13.16:

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

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

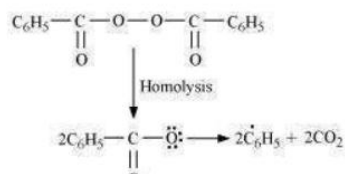


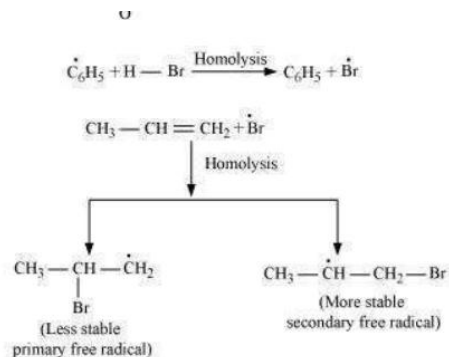
Secondary carbocations are more stable than primary carbocations. Hence, the secondary carbocations predominates since it forms at a faster rate as compared to primary carbocations. Thus, in the next step, Br^- attacks the primary carbocation to form 2-bromopropane as the major product.



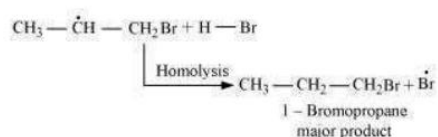
This reaction follows Markovnikov's rule where the negative part of the addendum is attached to the carbon atom having a less number of hydrogen atoms than other carbon atoms present in the compound.

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 more stable than primary radicals. Hence, the secondary radical predominates since it forms at a faster rate than the primary radical. Thus, 1-bromopropane is obtained as the major product.



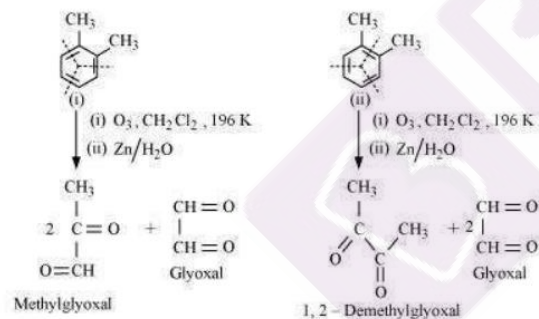
In the presence of peroxide, Br as free radical acts as an electrophile. Hence, two different products are obtained on addition of HBr to propene in the presence and absence of peroxide.

Question 13.17:

Write down the mechanism of ozonolysis of 1, 2-dimethylbenzene (o-xylene). Also show how does the result support Kekulé structure for benzene?

Answer 13.17:

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



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

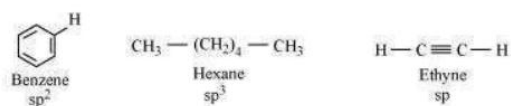
Question 13.18:

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, the electronegativity of carbon decreases and the electrons of C-H bond pair lie away from the carbon atom. As a result, the partial positive charge of H- atom 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 nucleophilic substitutions with difficulty and electrophilic substitution reactions easily?

Answer 13.19:

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

Therefore, benzene undergoes electrophilic substitution reactions very easily. On the other hand, Nucleophiles are also electron-rich species. Hence, they are repelled by benzene as compared to electrophiles. Hence, benzene undergoes nucleophilic substitutions with difficulty.

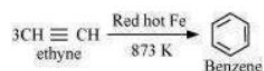
Question 13.20:

How would you make benzene from the following compounds?

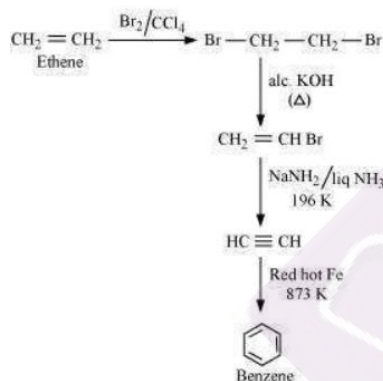
(i) Ethyne (ii) Ethene (iii) Hexane

Answer 13.20:

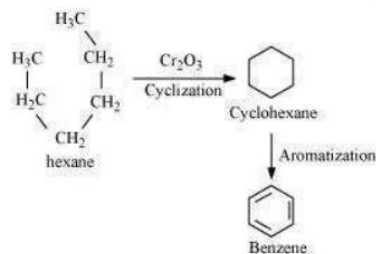
(i) Benzene from Ethyne:



(ii) Benzene from Ethene:



(iii) Hexane to Benzene



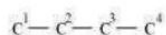
Question 13.21:

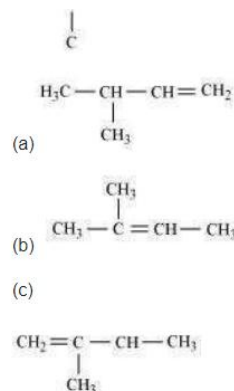
Write structures of all the alkenes which on hydrogenation give 2-methylbutane.

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:





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) $p\text{-H}_3\text{C}-\text{C}_6\text{H}_4-\text{NO}_2$, Toluene, $p\text{-O}_2\text{N}-\text{C}_6\text{H}_4-\text{NO}_2$.

Answer 13.22:

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^+ (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.

Hence, toluene has the maximum electron density and is most easily attacked by E^+ . Since NO_2 – is an electron withdrawing group. Hence, when the number of NO_2 – substituents is greater, the order is as follows:

$p\text{-O}_2\text{N}-\text{C}_6\text{H}_4-\text{NO}_2 < p\text{-H}_3\text{C}-\text{C}_6\text{H}_4-\text{NO}_2 < \text{Toluene}$.

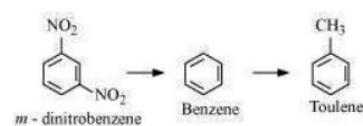
Question 13.23:

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:

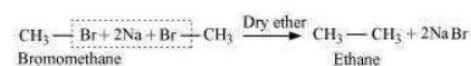
List the names of some Lewis acid which can be used during ethylation of benzene in a Friedel-Craft alkylation reaction.

The reaction of benzene with an acyl halide or acid anhydride in the presence of Lewis acids (AlCl_3) yields acyl benzene (or benzene ring). Such a reaction is called a Friedel-Craft alkylation reaction. This reaction takes place in the presence of a Lewis acid.

Question 13.25:

Answer 13.25

Example:


$$\begin{array}{ccc}
 \text{CH}_3 - \boxed{\text{I}} + 2\text{Na} + \boxed{\text{I}} - \text{CH}_2\text{CH}_3 & & \text{Iodomethane} \quad \quad \quad \text{Iodoethane} \\
 \downarrow \text{Dry ether} & & \\
 \text{CH}_3 - \text{CH}_2\text{CH}_3 + 2\text{NaI} & & \\
 \text{CH}_3 - \boxed{\text{I}} + 2\text{Na} + \boxed{\text{I}} - \text{CH}_3 & \xrightarrow{\text{Dry ether}} & 2\text{NaI} + \text{CH}_3 - \text{CH}_3 \\
 & & \text{Ethane} \\
 \text{CH}_3\text{CH}_2 - \boxed{\text{I}} + 2\text{Na} + \boxed{\text{I}} - \text{CH}_2\text{CH}_3 & \xrightarrow{\text{Dry ether}} & 2\text{NaI} + \text{CH}_3\text{CH}_2 - \text{CH}_2\text{CH}_3 \\
 & & \text{Butane}
 \end{array}$$

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