Hydrocarbons

9
Chapter

Exercise

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

Ans: Chlorination of methane proceeds by free radical chain mechanism which involves three steps as follows:

- Initiation:
  The reaction begins with the homolytic bond cleavage within Cl – Cl bond that results in the formation of chlorine free radicals as;

$$Cl-Cl \xrightarrow{h\upsilon} \dot{Cl} + \dot{Cl}$$

- Propagation:
  In this step, chlorine free radicals formed in the prior step abstracts a hydrogen atom from methane to generate methyl radicals as;

$$\underset{\text{Methane}}{CH_4} + \dot{Cl} \xrightarrow{h\upsilon} \dot{C}H_3 + H-Cl$$

The above methyl radicals then react with chlorine molecule to form methyl chloride along with the liberation of a chlorine free radical.

$$\dot{C}H_3 + Cl-Cl \longrightarrow \underset{\text{Methyl Chloride}}{H_3C-Cl} + \dot{Cl}$$

Thus, methyl and chlorine free radicals set up a chain reaction. When HCl and CH_3Cl are formed as major products, other higher halogenated compounds are also formed as follows;

$$H_3C-Cl + \dot{Cl} \longrightarrow H_2\dot{C}-Cl + HCl$$

$$H_2\dot{C}-Cl + Cl-Cl \longrightarrow CH_2Cl_2 + \dot{Cl}$$

- Termination:
  When all the reactants are consumed, the reaction stops and the chain gets to the point of termination. This happens by the combination of different free radicals.

Chlorine free radicals combine to form a chlorine molecule.

$$\dot{Cl} + \dot{Cl} \longrightarrow Cl—Cl$$

Methyl free radicals combine to form ethane.

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow \underset{\text{Ethane}}{H_3C—CH_3}$$

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

2. Write IUPAC names of the following compounds:

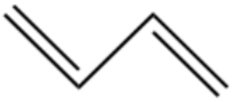
a. $CH_3CH{=}C(CH_3)_2$

Ans: The IUPAC name of the above compound is 2-Methylbut-2-ene.

b. $H_2C{=}CCH{\equiv}CCH_3$

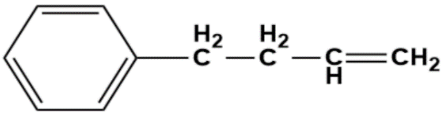
Ans: The IUPAC name of the above compound is Pen-1-en-3-yne.

c.



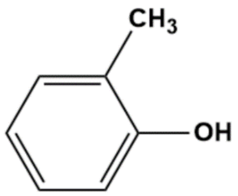
Ans: The IUPAC name of the above compound is Buta-1,3-diene or 1,3-Butadiene.

d.



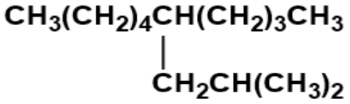
Ans: The IUPAC name of the above compound is 4-Phenylbut-1-ene.

e.



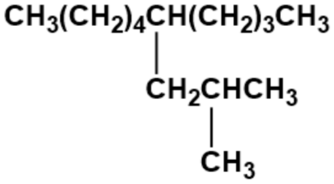
Ans: The IUPAC name of the above compound is 2-Methylphenol.

f.



$$CH_3(CH_2)_4\underset{\underset{\displaystyle CH_2CH(CH_3)_2}{|}}{C}H(CH_2)_3CH_3$$

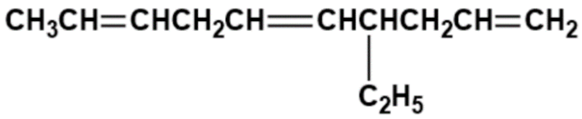
Ans: The above compound can be easily formulated as;



$$CH_3(CH_2)_4\underset{\underset{\displaystyle CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_3}{|}}{C}H(CH_2)_3CH_3$$

The IUPAC name of the above compound is 5-(2-Methylpropyl) decane.

g.



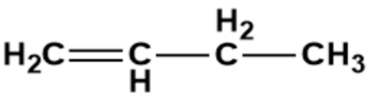
$$CH_3CH{=}CHCH_2CH{=}\underset{\underset{\displaystyle C_2H_5}{|}}{C}HCH_2CH{=}CH_2$$

Ans: The IUPAC name of the above compound is 4-Ethyldeca-1,5,8-triene.

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:

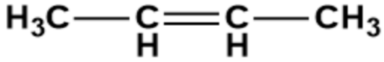
(a) C_4H_8 (one double bond)

Ans: The structures with their IUPAC names are given as;



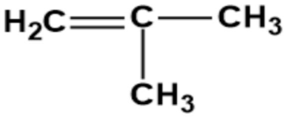
$$H_2C{=}\underset{H}{C}{-}\overset{H_2}{C}{-}CH_3$$

IUPAC name: But-1-ene



$H_3C-\underset{H}{C}=\underset{H}{C}-CH_3$

IUPAC name: But-2-ene

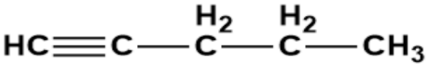


$H_2C=\underset{\overset{|}{CH_3}}{C}-CH_3$

IUPAC name: 2-Methylprop-1-ene

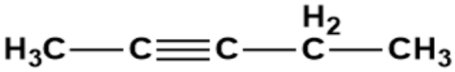
(b) C_5H_8 (one triple bond)

Ans: The structures with their IUPAC names are given as;



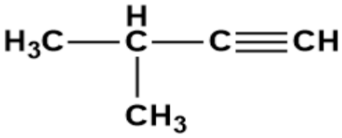
$HC\equiv C-\overset{H_2}{C}-\overset{H_2}{C}-CH_3$

IUPAC name: Pent-1-yne



$H_3C-C\equiv C-\overset{H_2}{C}-CH_3$

IUPAC name: Pent-2-yne



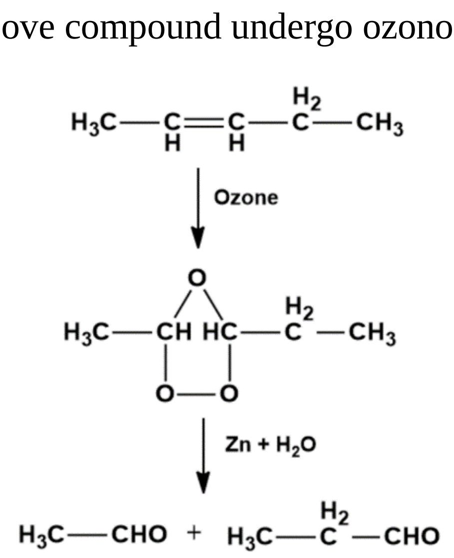
$H_3C-\overset{H}{\underset{\overset{|}{CH_3}}{C}}-C\equiv CH$

IUPAC name: 3-Methylbut-1-yne

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

(i) Pent-2-ene

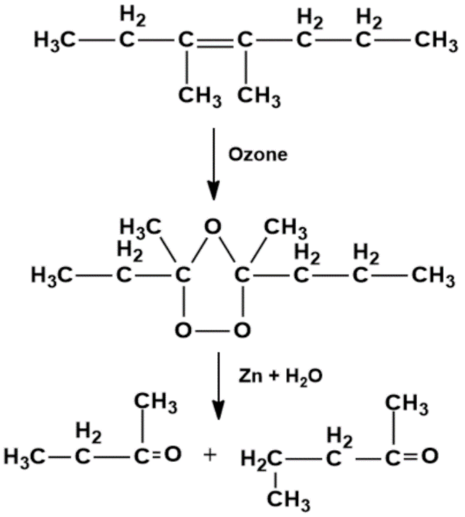
Ans: The above compound undergo ozonolysis as follows;



The products of the reaction are ethanal and propanal.

(ii) 3,4-Dimethyl-hept-3-ene

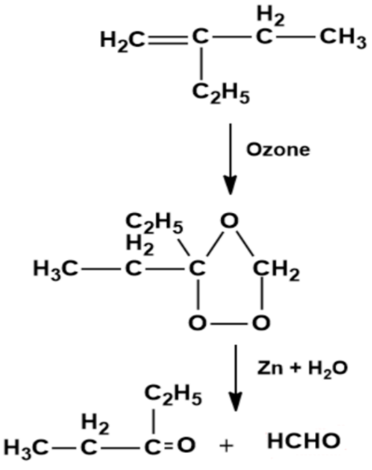
Ans: The above compound undergo ozonolysis as follows;



The products of reaction are Butan-2-one and Pentan-2-one.

(iii) 2-Ethylbut-1-ene

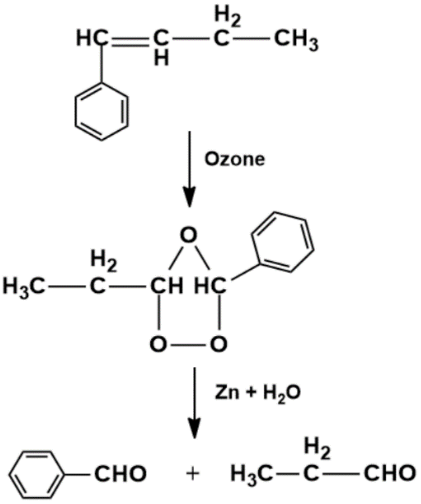
Ans: The above compound undergo ozonolysis as follows;



The products of the reaction are Pentan-3-one and methanal.

(iv) 1-Phenylbut-1-ene

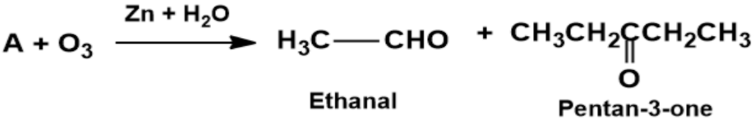
Ans: The above compound undergo ozonolysis as follows;



The products of the reaction are benzaldehyde and propanal.

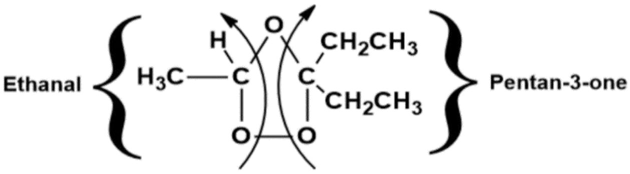
5. An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of 'A'.

Ans: According to the given data the following reaction format can be formed as:



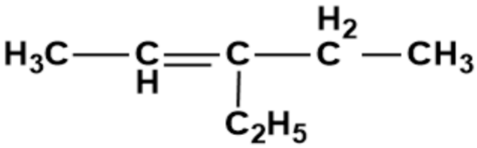
$$A + O_3 \xrightarrow{Zn + H_2O} H_3C-CHO + CH_3CH_2C(=O)CH_2CH_3$$

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



This ozonide is formed as an addition of ozone to reactant 'A'. Thus, the desired structure of 'A' can be obtained by the removal of ozone from the above ozonide.

The structural formula of 'A' is as follows;



$$H_3C-CH=C(C_2H_5)-CH_2-CH_3$$

The IUPAC name of the above compound is 3-Ethylpent-2-ene.

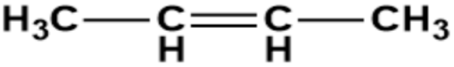
6. An alkene ‘A’ contains three C – C, eight C – H σ bonds and one C – C π bond. ‘A’ on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write IUPAC name of ‘A’.

Ans: According to 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 8 C–H σ bonds which state that there are 8 hydrogen atoms in ‘A’. Also, there are 3 C–C bonds which state that there are 4 carbon atoms present in the same.

Combining the information given, the structure of ‘A’ can be represented as:

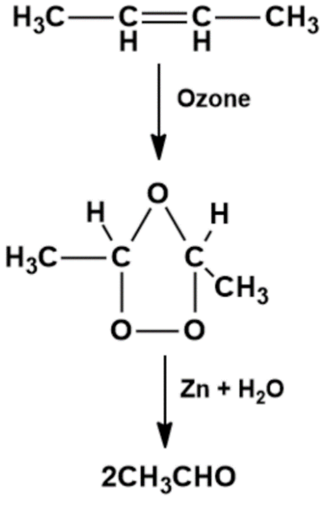


$$H_3C-\underset{H}{C}=\underset{H}{C}-CH_3$$

‘A’ has 3 C-C bonds, 8 C-H σ bonds along with a C-C π bond which states that the IUPAC name of the same is But-2-ene.

Now,

Ozonolysis of ‘A’ takes place as;

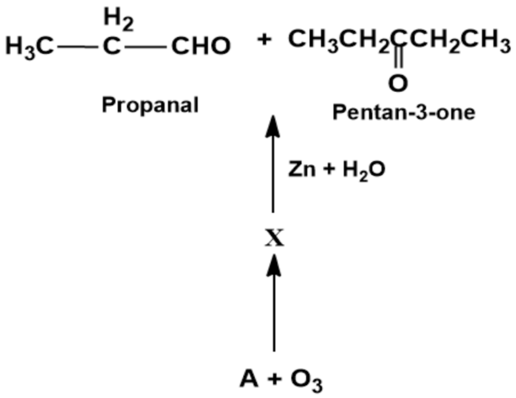


Here, we can say that the final product is being proved as ethanal with molar mass 44u.

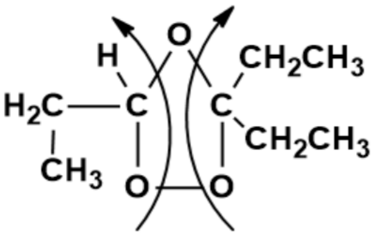
7. Propanal and pentan-3-one are the ozonolysis products of an alkene? What is the structural formula of the alkene?

Ans: According to the given information, propanal and pentan-3-one are the ozonolysis products of an alkene. Consider the given alkene as ‘A’.

Now, writing the reverse of the ozonolysis reaction, we get;

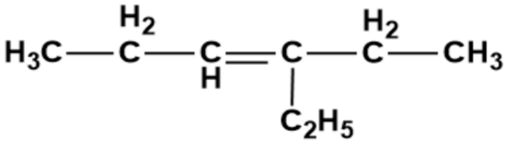


The products are obtained on the cleavage of ozonide ‘X’. Thus, ‘X’ contains both products in cyclic form. The possible structure of ozonide can be represented as follows;



X

We know that, ‘X’ is an addition product of alkene ‘A’ with ozone. Thus, the possible structure of alkene ‘A’ is:



$$H_3C-\overset{H_2}{C}-\underset{H}{C}=\underset{C_2H_5}{\underset{|}{C}}-\overset{H_2}{C}-CH_3$$

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

(i) Butane

Ans: The combustion reaction is given as;

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

(ii) Pentene

Ans: The combustion reaction is given as;

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

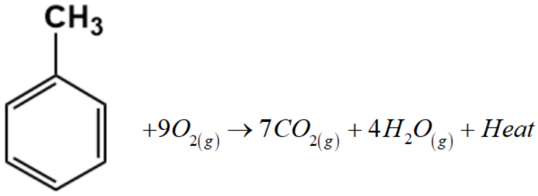
(iii) Hexyne

Ans: The combustion reaction is given as;

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

(iv)Toluene

Ans: The combustion reaction is given as;



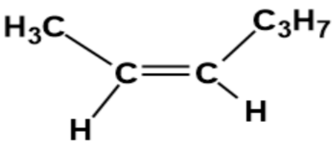
Toluene

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

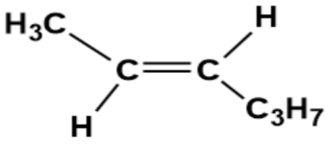
Ans:

Hex-2-ene is represented as $CH_3-CH=CH-CH_2-CH_2-CH_3$.

Geometrical isomers of hex-2-ene are:



cis-Hex-2-ene



trans-Hex-2-ene

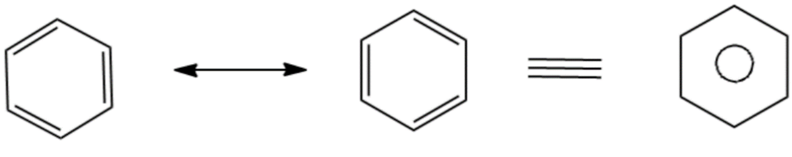
The dipole moment of cis-compound is a sum of the dipole moments of $C-CH_3$ and $C-CH_2CH_2CH_3$ bonds acting in the same direction. The dipole moment of a trans-compound is the resultant of the dipole moments of the same bonds acting in opposite directions.

Thus, cis-isomer is more polar than trans-isomer. The higher the polarity, the greater is the intermolecular dipole-dipole interaction and the higher will be the boiling point.

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

10. Why is benzene extraordinarily stable though it contains three double bonds?

Ans: Benzene has resonating structures which define its stability perfectly. They can be represented as;



All 6 carbon atoms in benzene are sp^2 hybridized. The 2 sp^2 hybrid orbitals of each carbon atom overlaps with the sp^2 hybrid orbitals of adjacent carbon atoms to form 6 σ bonds in the hexagonal plane. The remaining sp^2 hybrid orbital on each carbon atom overlaps with the *s*-orbital of hydrogen to form 6 sigma C–H bonds. The remaining unhybridized *p*-orbital of carbon atoms has the possibility of forming 3 π bonds by the lateral overlap of adjacent C atoms.

The 6 π electrons are delocalized and can move freely about the 6 carbon nuclei. Even after the presence of 3 double bonds, these delocalized π-electrons stabilize benzene.

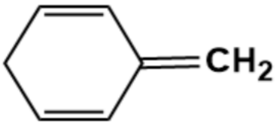
11. What are the necessary conditions for any system to be aromatic?

Ans: A compound is only said to be aromatic if it completely satisfies the following conditions;

- It should have a planar structure and should be cyclic.
- The π-electrons of the compound must be completely delocalized in the ring.
- The total number of π-electrons present in the ring should be equal to (4n+ 2), where n = 0, 1, 2 … etc. {Huckel's rule}.

12. Explain why the following systems are not aromatic?

(i)



Ans: In the given compound, one carbon atom is sp^3 hybridized which signifies that it is tetrahedral (not planar). As for the compound to be aromatic, it should be planar. Thus, the given compound is not aromatic in nature.

(ii)

Ans: In the given compound, one carbon atom is sp^3 hybridized which signifies that it is tetrahedral (not planar). As for the compound to be aromatic, it should be planar.

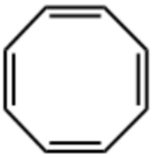
Also, for the given compound, the number of $\pi-$ electrons is 4 so, by Huckel's rule;

$$4n+2=4$$

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

For a compound to be aromatic, the value of n must be an integer i.e. 0, 1, 2… etc. which is not satisfied for the given compound. Therefore, it is not aromatic in nature.

(iii)



Ans: For the given compound, the number of $\pi-$electrons is 8 so, by Huckel's rule;

$$4n+2=8$$

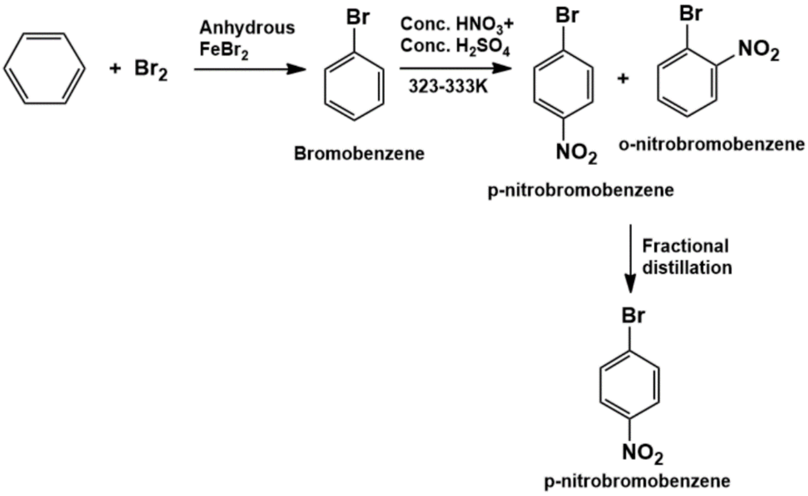
$$n=\frac{2}{3}$$

For a compound to be aromatic, the value of n must be an integer i.e. 0, 1, 2… etc. which is not satisfied for the given compound. Therefore, it is not aromatic in nature.

13. How will you convert benzene into

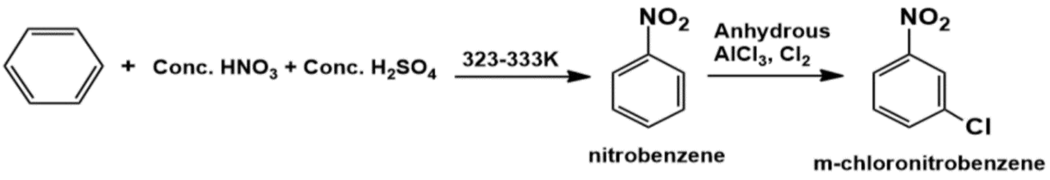
(i) p-nitrobromobenzene

Ans: The reactions are given as;



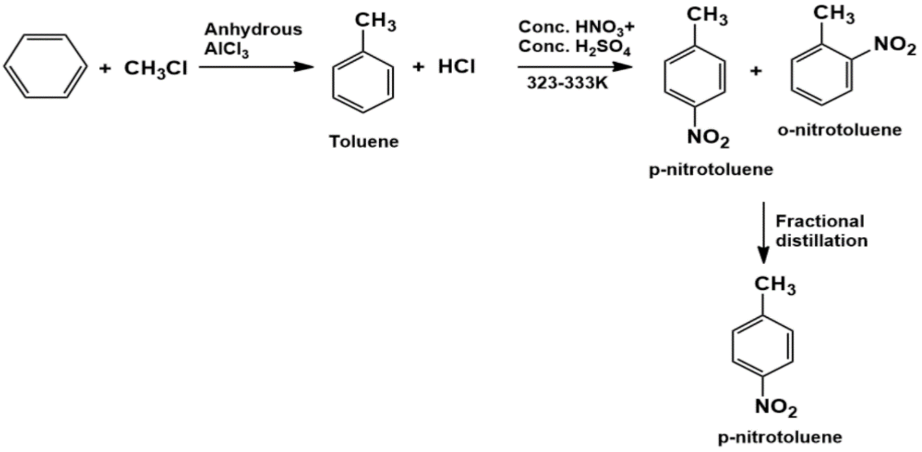
(ii) m-nitrochlorobenzene

Ans: The reactions are given as;



(iii)p -nitrotoluene

Ans: The reactions are given as;

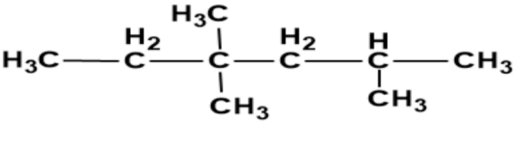


(iv) acetophenone

Ans: The reactions are given as;

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

Ans: The given alkane can be represented as;



- Primary carbon atoms are those which are bonded to only one carbon atom or none. i.e., they have only 1 carbon atom as their neighbor or none (in case of methane). The given structure has 5 primary carbon atoms and 15 hydrogen atoms attached to it.
- Secondary carbon atoms are those which are bonded to 2 carbon atoms i.e., they have 2 carbon atoms as their neighbors. The given structure has 2 secondary carbon atoms and 4 hydrogen atoms attached to it.
- Tertiary carbon atoms are those which are bonded to 3 carbon atoms i.e., they have 3 carbon atoms as their neighbors. The given structure has 1 tertiary carbon atom and only 1 hydrogen atom is attached to it.

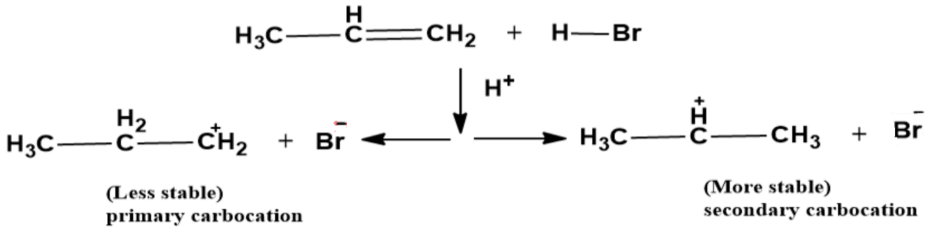
15. What effect does branching of an alkane chain have on its boiling point?

Ans: Alkanes mainly experience intermolecular Van der Waals forces. The stronger the force, the greater the boiling point of the alkane.

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

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 a mechanism.

Ans: 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 primary and secondary carbocations as shown:



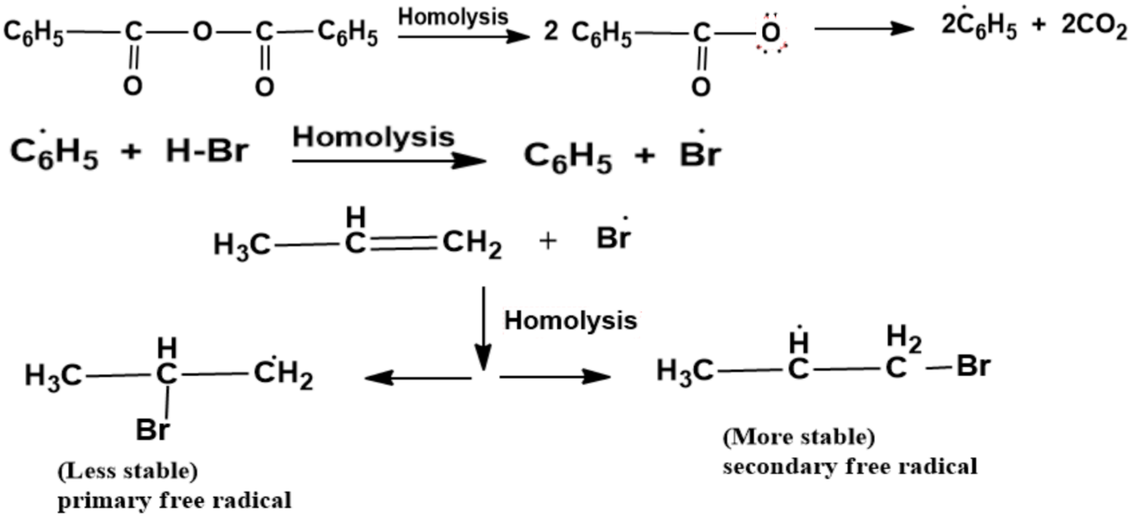
Secondary carbocations are comparatively more stable than primary carbocations. Thus, the former predominates since it will form at a faster rate. Thus, now Br^- attacks the carbocation to form 2 – bromopropane as the major product.

2-Bromopropane

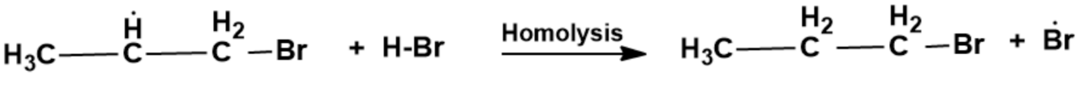
This reaction follows Markovnikov’s rule.

Now,

In the presence of benzoyl peroxide, an additional reaction takes place by anti-Markovnikov’s rule. The reaction follows a free radical chain mechanism as;



Here, 1 – bromopropane is obtained as the major product.

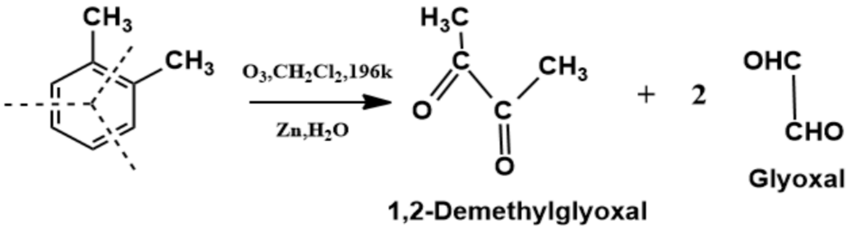


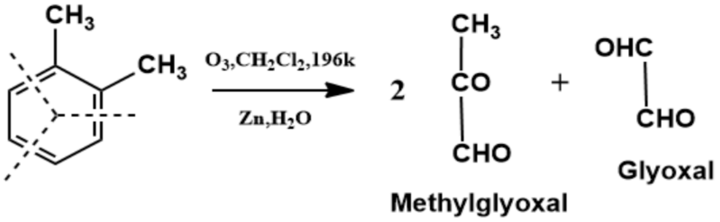
1-Bromopropane
(major product)

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

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

Ans: o-xylene has two resonating structures showing different reactions as follows;

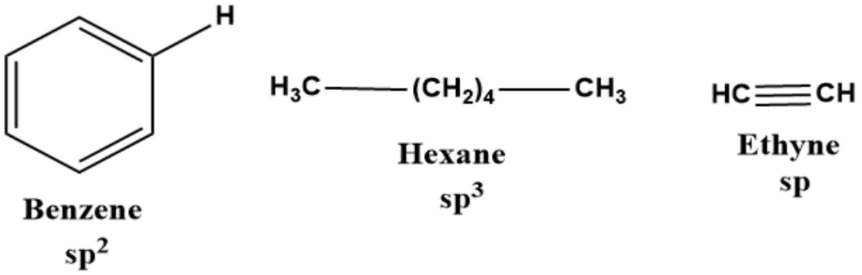




The three products are formed i.e., methyl glyoxal, 1,2-demethylglyoxal, and glyoxal from two Kekule structures. Since all three products cannot be obtained from any one of the two structures, this proves that o-xylene is a resonance hybrid of two Kekule structures.

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

Ans: Acidic character of any species is defined on the basis of its ease with which it can lose the H– atoms. The hybridization state of carbon in the given compound is given as;



According to the hybridization criterion, as the s–character increases the electronegativity of carbon increases and the electrons of C–H bond pair lie closer to the C atom.

The s–character increases in the order:

$sp^3 < sp^2 < sp$

Thus, the decreasing order of acidic behavior is Ethyne > Benzene > Hexane.

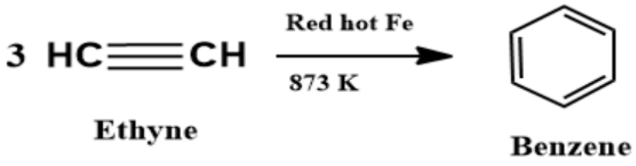
19. Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?

Ans: Benzene is a planar molecule having delocalized electrons above and below the plane of the ring. Thus, this makes it electron-rich. As a result, it is highly attractive to electron deficient species i.e., electrophiles. This is the reason; benzene undergoes electrophilic substitution reactions very easily. Whereas, nucleophiles are electron-rich. Hence, they are repelled by benzene. Therefore, benzene undergoes nucleophilic substitutions with much difficulty.

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

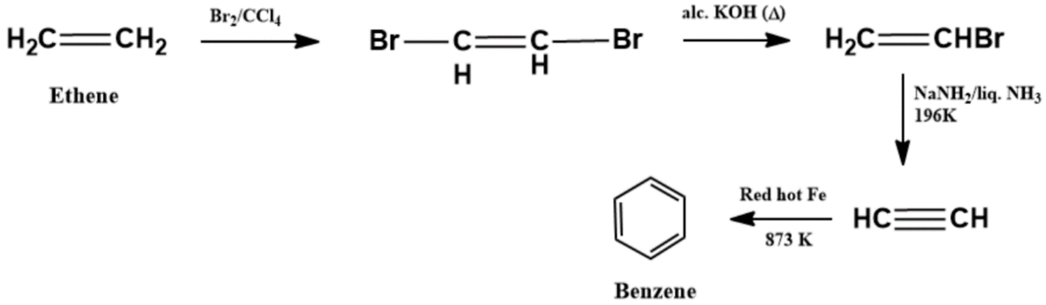
(i) Ethyne

Ans: The reactions are given as;



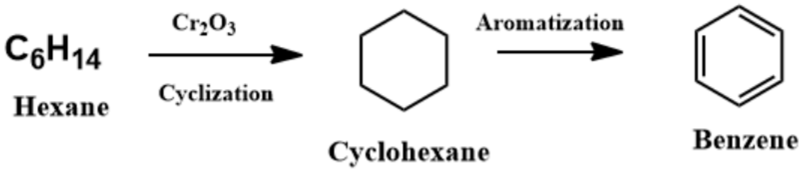
(ii) Ethene

Ans: The reactions are given as;



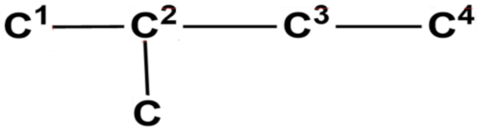
(iii) Hexane

Ans: The reactions are given as;

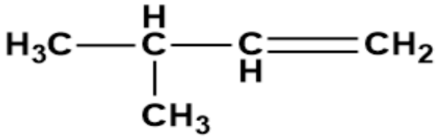


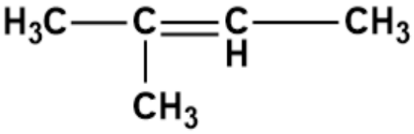
21. Write structures of all the alkenes which on hydrogenation give 2-methylbutane.

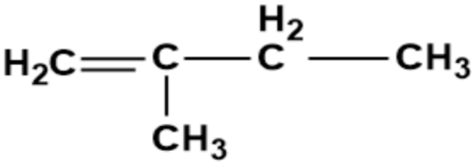
Ans: The structure of 2-methylbutane can be stated as (skeleton);



On the basis of the above structure, various alkenes that will give 2-methylbutane on hydrogenation are given as;







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

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

The higher the electron density on a benzene ring, the more reactive is the compound towards an electrophile.

Here,

The presence of an EWG deactivates the aromatic ring by decreasing the electron density. Now, as the NO_2^{-2}group is more EWG that Cl^- group.

Thus, the decreasing order of EWG is given as;

Chlorobenzene > p-nitrochlorobenzene > 2,4-dinitrochlorobenzene

(b) Toluene, $p-CH_3-C_6H_4-NO_2$, $p-O_2N-C_6H_4-NO_2$.

Ans: Here, CH_3^- is an EDG and NO_2^- is an EWG.

Thus, toluene will have the maximum electron density and is most easily attacked by E^+ .

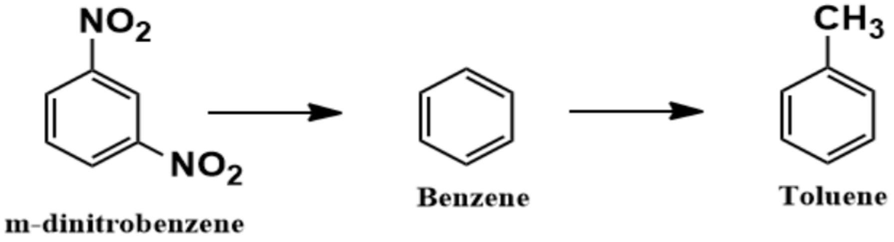
The number of NO_2^- substituents define the order as;

Toluene > $p-CH_3-C_6H_4-NO_2$ > $p-O_2N-C_6H_4-NO_2$

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

Ans: 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_2^+).

Now as we know, CH_3^- group is electron donating and NO_2^- is electron withdrawing. Therefore, toluene will have the maximum electron density among the 3 compounds followed by benzene. On the other hand, m–Dinitrobenzene will have the least electron density. Thus, it will undergo nitration with difficulty. Hence, the increasing order of nitration is as;



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

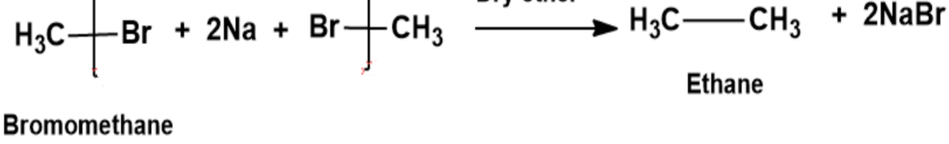
Ans: The ethylation reaction of benzene involves the addition of an ethyl group on the benzene ring. This reaction is called Friedel-Craft alkylation reaction and takes place in the presence of a Lewis acid.

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

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

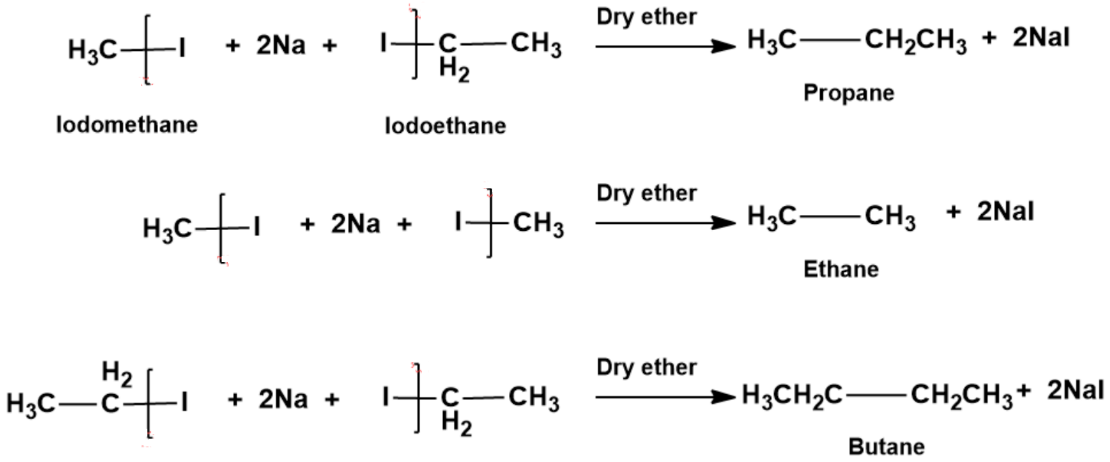
Ans: Wurtz reaction is limited for the synthesis of symmetrical alkanes (alkanes with an even number of carbon atoms). In the reaction, two similar alkyl halides are taken as reactants and an alkane, containing double the number of carbon atoms, are formed.

Example:



This 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.

Example:



The boiling points of the above alkanes are very close. Hence, it becomes difficult to separate them.