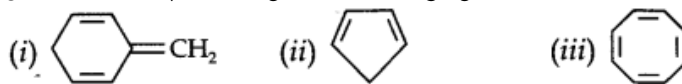
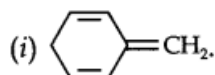




Question 12. Explain why the following systems are not aromatic?

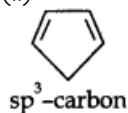


Answer:



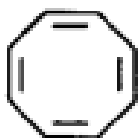
Due to the presence of a sp^3 -hybridized carbon, the system is not planar. It does contain six π -electrons but the system is not fully conjugated since all the six π -electrons do not form a single cyclic electron cloud which surrounds all the atoms of the ring. Therefore, it is not an aromatic compound.

(ii)



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

(iii)



Planar



Tub shaped

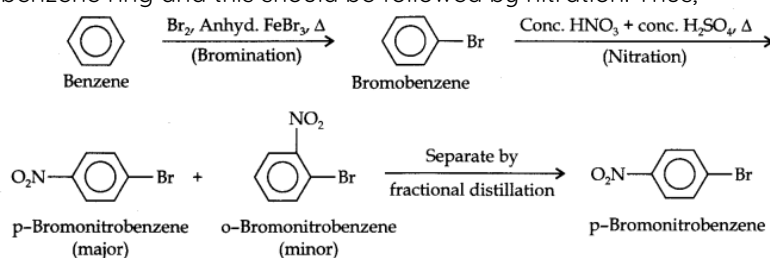
Cyclo-octatetraene is not planar but is tub shaped. It is, therefore, a non-planar system having 8 π -electrons.

Therefore, the molecule is not aromatic since it does not contain a planar cyclic cloud having $(4n + 2)$ π -electrons.

Question 13. How will you convert benzene into (i) p-nitrobromobenzene (ii) m-nitrochlorobenzene (iii) p-nitrotoluene (iv) acetophenone?

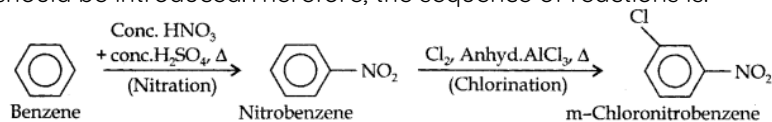
Answer:

(i) The two substituents in the benzene ring are present at p-positions. Therefore, the sequence of reactions should be such that first an o, p-directing group, i.e., Br atom should be introduced in the benzene ring and this should be followed by nitration. Thus,

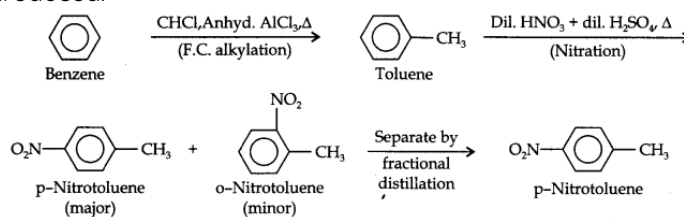


(ii) Here since the two substituents are at p-position w.r.t. each other, therefore, the first substituent in the benzene ring should be an o, p-directing group (i.e., CH_3) and then the other group (i.e., NO_2)

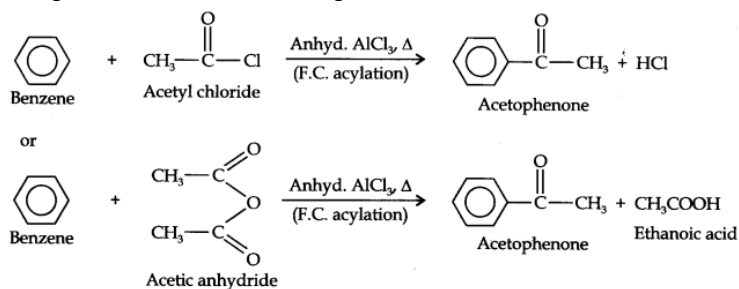
should be introduced. Therefore, the sequence of reactions is:



(iii) Here since the two substituents are at m-position w.r.t. each other, therefore, the first substituent in the benzene ring should be a m-directing group (i.e., NO₂) and then other group (i.e., Cl) should be introduced.

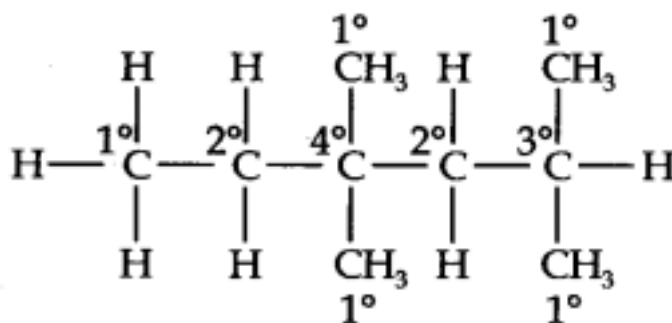


(iv) Acetophenone can be prepared by F.C. acylation using either acetyl chloride or acetic anhydride.



Question 14. In the alkane, CH₃CH₂—C(CH₃)₂—CH₂—CH(CH₃)₂, identify 1°, 2°, 3° carbon atoms and give the number of H-atoms bonded to each one of these.

Answer: The expanded formula of the given compound is

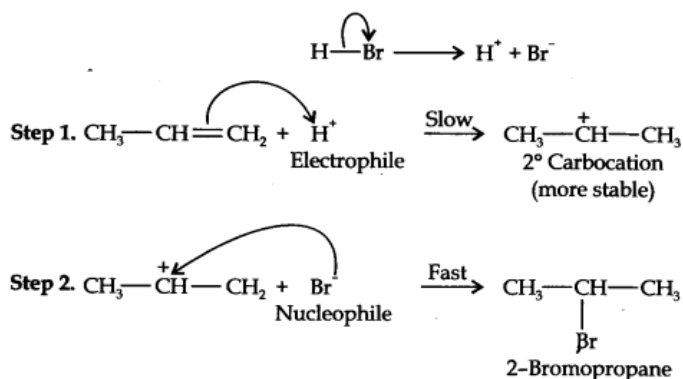


Question 15. What effect does branching of an alkane chain has on its boiling point?

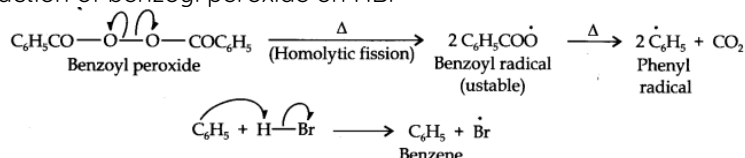
Answer: Branching of carbon atom chain decreases the boiling point of alkane.

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

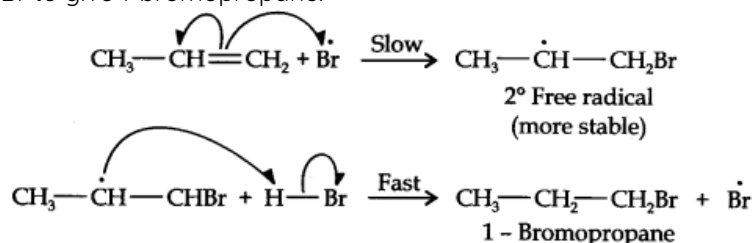
Answer: Addition of HBr to propene is an ionic electrophilic addition reaction in which the electrophile, i.e., H⁺ first adds to give a more stable 2° carbocation. In the 2nd step, the carbocation is rapidly attacked by the nucleophile Br[−] ion to give 2-bromopropane.



In presence of benzoyl peroxide, the reaction is still electrophilic but the electrophile here is a Br free radical which is obtained by the action of benzoyl peroxide on HBr



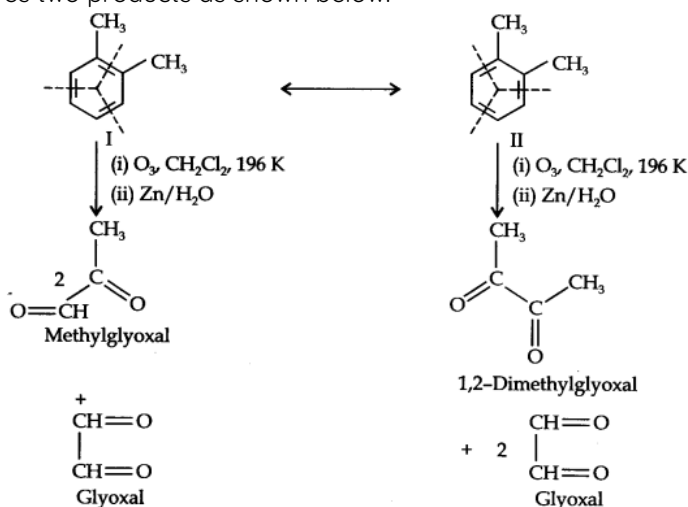
In the first step, Br radical adds to propene in such a way so as to generate the more stable 2° free radical. In the second step, the free radical thus obtained rapidly abstracts a hydrogen atom from HBr to give 1-bromopropane.



From the above discussion, it is evident that although both reactions are electrophilic addition reactions but it is due to different order of addition of H and Br atoms which gives different products.

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

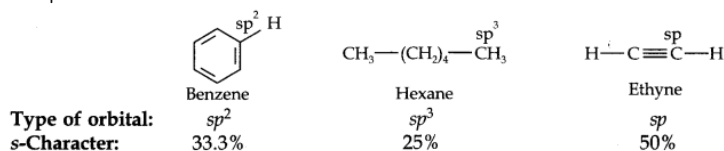
Answer: o-Xylene may be regarded as a resonance hybrid of the following two Kekule structures. Ozonolysis of each one of these gives two products as shown below:



Thus, in all, three products are formed. Since all the three products cannot be obtained from any one of the two Kekule structures, this shows that o-xylene is a resonance hybrid of the 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 behaviour.

Answer: The hybridization state of carbon in these three compounds is:



Since s-electrons are closer to the nucleus, therefore, as the s-character of the orbital making the C—H bond increases, the electrons of C—H bond lie closer and closer to the carbon atom. In other words, the partial +ve charge on the H-atom and hence the acidic character increases as the s-character of the orbital increases. Thus, the acidic character decreases in the order: Ethyne > Benzene > Hexane.

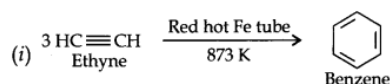
Question 19. Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?

Answer: Due to the presence of an electron cloud containing 6 π -electrons above and below the plane of the ring, benzene is a rich source of electrons. Consequently, it attracts the electrophiles (electron-deficient) reagents towards it and repels nucleophiles (electron-rich) reagents. As a result, benzene undergoes electrophilic substitution reactions easily and nucleophilic substitutions with difficulty.

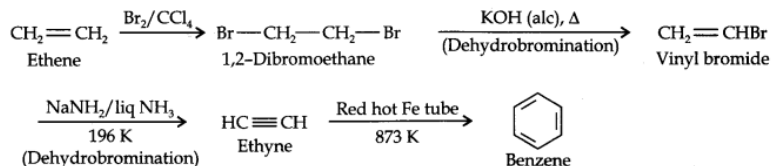
Question 20. How will you convert the following compounds into benzene?

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

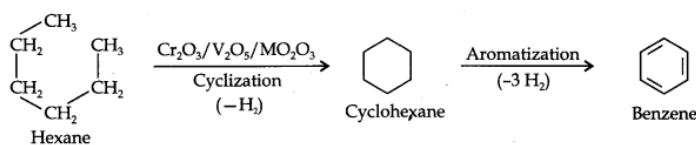
Answer:



(ii) Ethene is first converted into ethyne and then to benzene as shown above.



(iii) When vapours of hexane are passed over heated catalyst consisting of Cr_2O_3 , MO_2O_3 and V_2O_5 at 773 K under 10-20 atm pressure, cyclization and aromatization occurs simultaneously to afford benzene

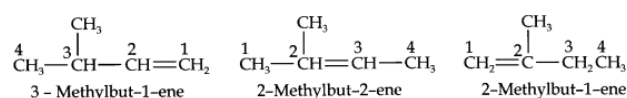


Question 21. Write structures of all the alkenes which on hydrogenation give 2-methylbutane.

Answer:

The basic skeleton 2-methylbutane is $\text{C}^1-\text{C}^2(\text{CH}_3)-\text{C}^3-\text{C}^4$

Putting double bonds at various different positions and satisfying the tetravalency of each carbon, the structures of various alkenes which give 2-methylbutane on hydrogenation are:



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

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

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

Answer:

(a) The typical reactions of benzene are electrophilic substitution

reactions. Higher the electron-density in the benzene ring, more reactive is the compound towards these reactions. Since NO₂ is a more powerful electron-withdrawing group than Cl, therefore, more the number of nitro groups, less reactive is the compound. Thus, the overall reactivity decreases in the order:

Chlorobenzene > p-nitrochlorobenzene > 2, 4-dinitrochlorobenzene
 (b) Here, CH₃ group is electron donating but NO₂ group is electron-withdrawing. Therefore, the maximum electron-density will be in toluene, followed by p-nitrotoluene followed by p-dinitrobenzene. Thus, the overall reactivity decreases in the order:
 Toluene > p-H₃C-C₆H₄-NO₂, p-O₂N-C₆H₄-NO₂.

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

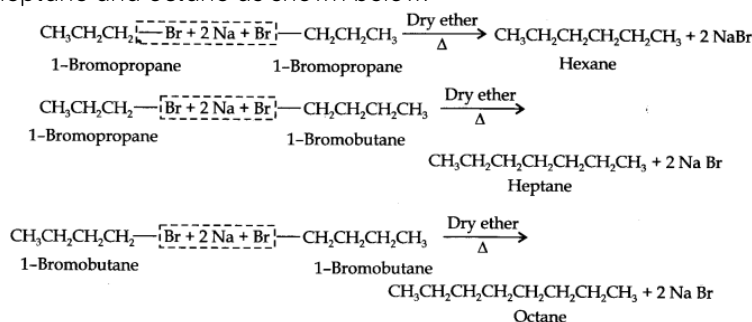
Answer: CH₃ group is electron-donating while -NO₂ group is electron-withdrawing. Therefore, maximum electron density will be in toluene, followed by benzene and least in m-dinitrobenzene. Therefore, the ease of nitration decreases in the order: toluene > benzene > m-dinitrobenzene.

Question 24. Suggest the name of another Lewis acid instead of anhydrous aluminium chloride which can be used during ethylation of benzene.

Answer: Anhydrous Ferric Chloride (FeCl₃) is another Lewis acid which can be used.

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

Answer: For preparation of alkanes containing odd number of carbon atoms, a mixture of two alkyl halides has to be used. Since two alkyl halides can react in three different ways, therefore, a mixture of three alkanes instead of the desired alkane would be formed. For example, Wurtz reaction between 1-bromopropane and 1-bromobutane gives a mixture of three alkanes i.e., hexane, heptane and octane as shown below:



***** END *****