

Ncert problems and solutions

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

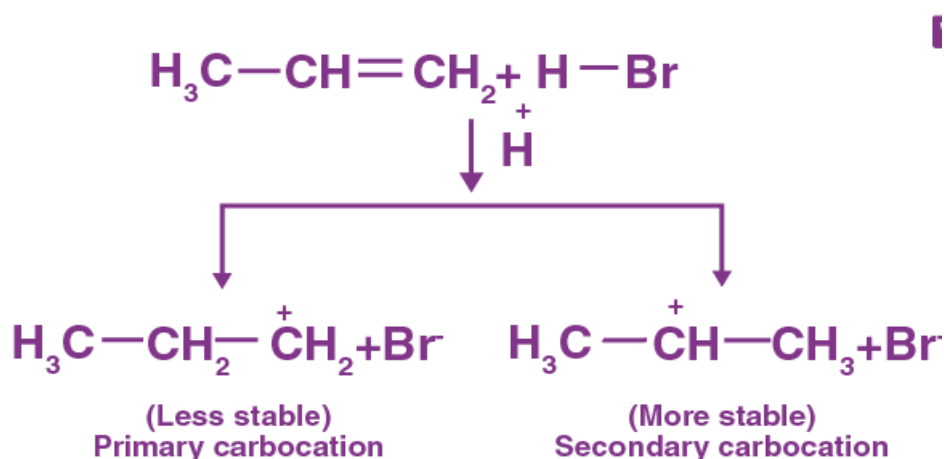
Alkanes encounter Van-der Waals forces between molecules. The higher the alkane's power, the greater is the boiling point.

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

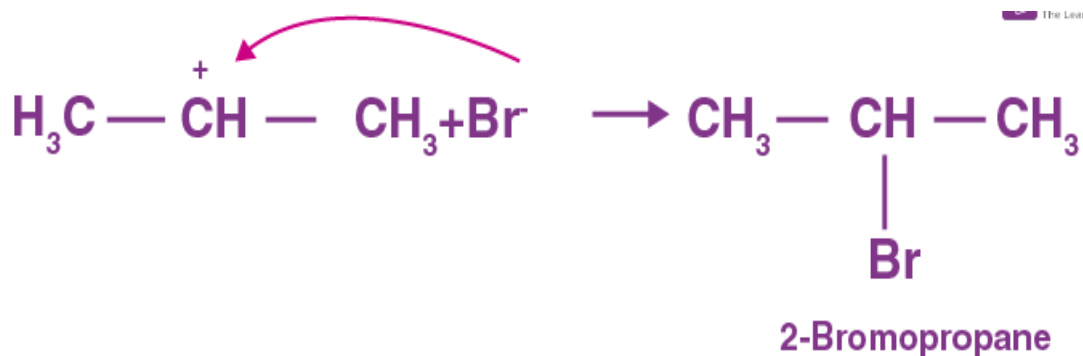
Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism.

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

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

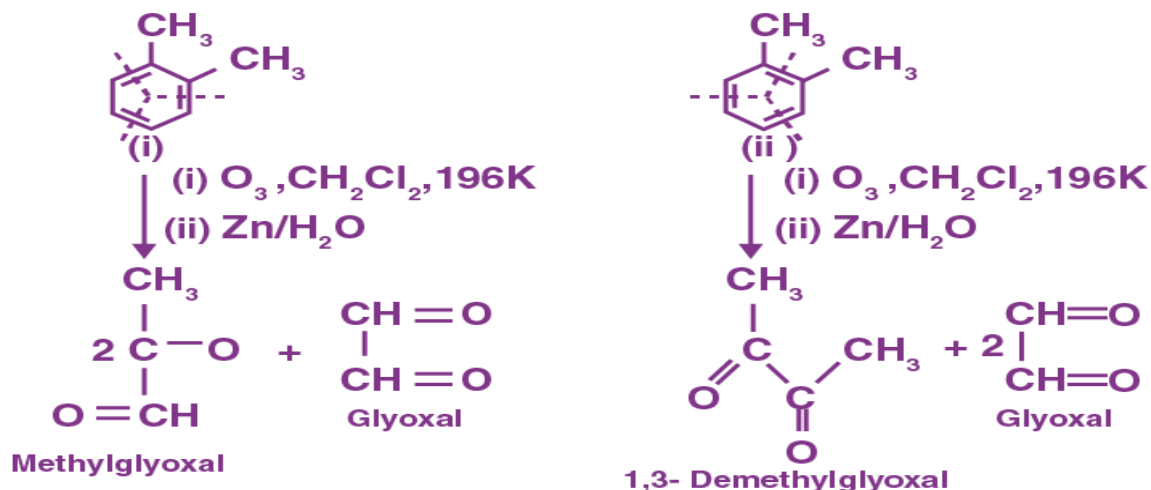


Secondary carbocations are stable in comparison with primary carbocations. The secondary carbocations therefore predominate, as they form at a faster rate than primary carbocations. Thus, Br⁻ attacks the primary carbocation to form 2-bromopropane as the main product in the next step.



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

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

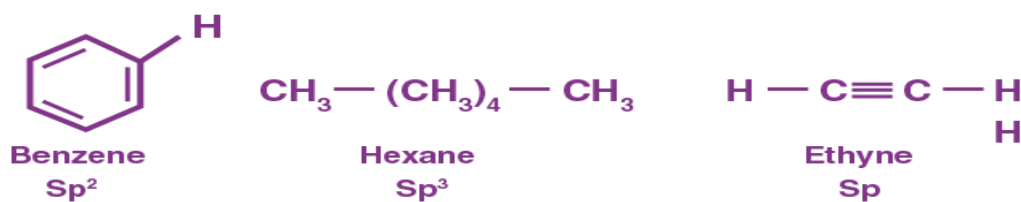


All three products are obtained from two Kekulé structures of o-xylene, i.e., methyl glyoxal, 1, 2-demethylglyoxal, and glyoxal. As all three products can not be obtained from either of the two structures, this proves that o-xylene is a resonance hybrid of two Kekulé (I and II) structures.

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

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

The hybridization state of carbon in the given compound is:



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

The s-character decreases in the order:



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

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

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

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

Question 13.20:

How would you convert the following compounds into benzene?

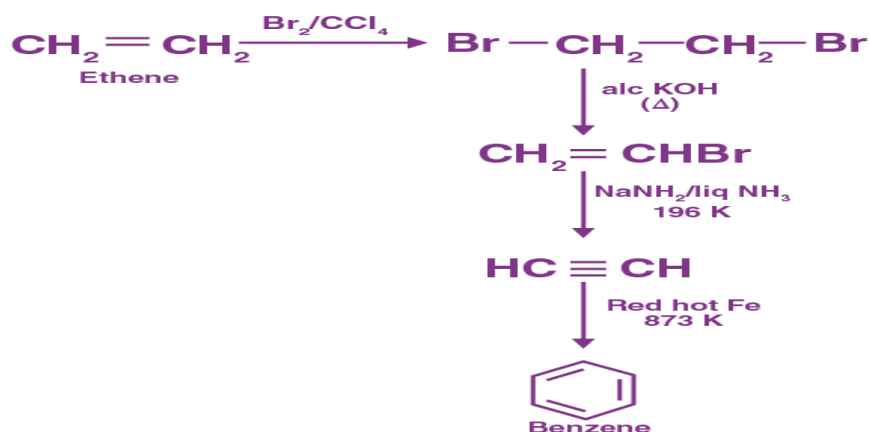
(i) Ethyne (ii) Ethene (iii) Hexane

Answer 13.20:

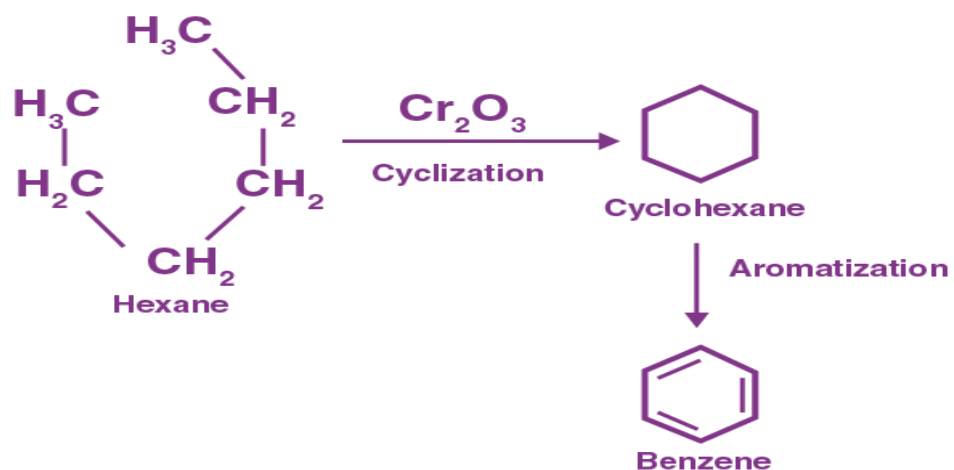
(i) Benzene from Ethyne:



(ii) Benzene from Ethene:



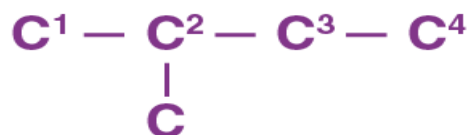
(iii) Hexane to Benzene



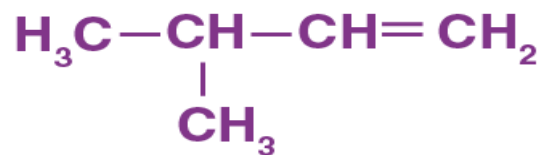
Write structures of all the alkenes which on hydrogenation give 2-methylbutane.

The basic structure of 2-methylbutane is shown below:

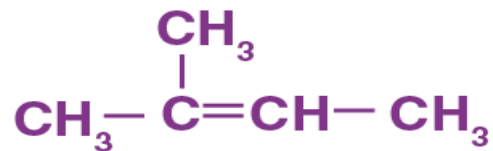
On the basis of the above structure, various alkenes that will give 2-methylbutane on hydrogenation are shown below:



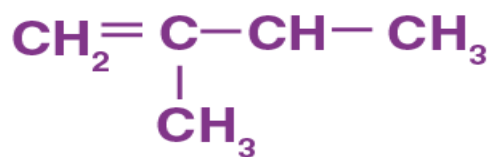
(a)



(b)



(c)



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*- $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{NO}_2$.

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

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

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

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

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

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

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

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

Out of benzene, *m*-dinitrobenzene and toluene, state the increasing order of nitration. Justify your 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 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:

