BP 202T - PHARMACEUTICAL ORGANIC CHEMISTRY - I

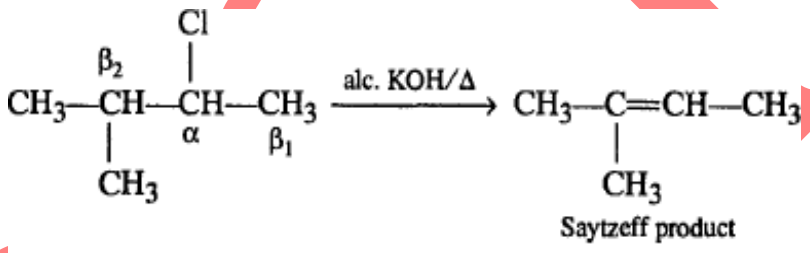
UNIT: 2 ALKANES, ALKENE & CONJUGATED DIENES

CLASS: 4

TOPIC: SAYTZEFF'S ORIENTATION AND REARRANGEMENT OF CARBOCATIONS

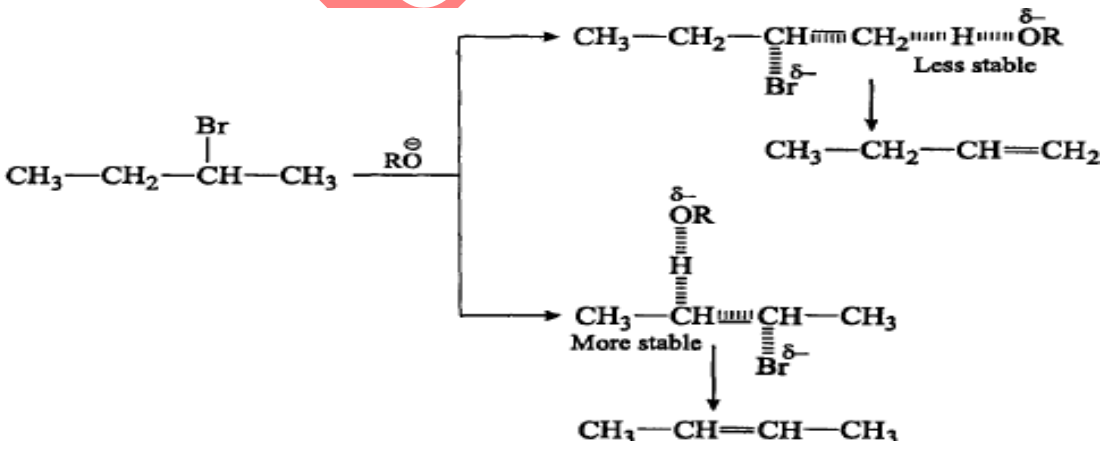
SAYTZEFF RULE (ZAITSEV RULE**):**

According to this rule, major product is the most substituted alkene, *i.e.*,the most stable alkene. Thus, the major product is obtained by elimination of H^+ from that β-carbon whichhas the least number of hydrogen. Product of the reaction in this case is known as Saytzeff product.



Theoretical Explanation for Saytzeff Rule

- Explanation for the more stable alkene (Saytzeff product) being formed in preference to the less stable alkene, is available from the transition states leading to these two alkenes.
- In either transition state, the removal of a proton and the formation of the double bond is taking place simultaneously.
- The transition state has some double-bond character which is represented by the dotted line.



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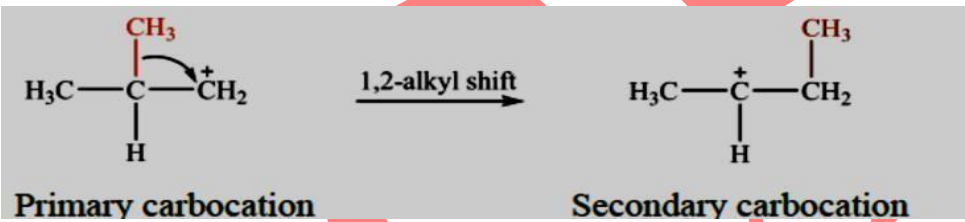
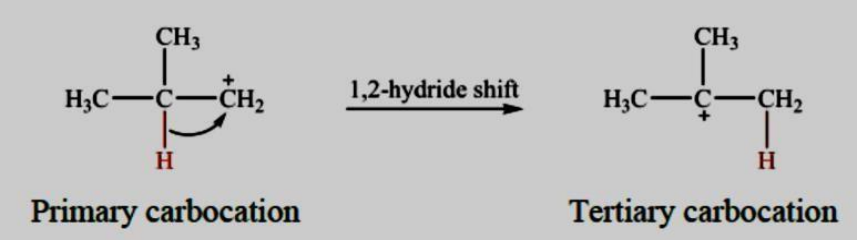
REARRANGEMENT OF CARBOCATION:

- The bonding electrons of a carbocation may shift between adjacent atoms to form a more stable carbocation.
- For example, rearrangement will occur if a secondary carbocation can be formed from a primary carbocation because a secondary carbocation is more stable than the primary carbocation.
- There can be two types of rearrangements-
  1. Shift of an alkyl group is called a 1, 2-alkyl shift.
  2. 1, 2-hydride shift
  - In the following example the migrating methyl group-



  - Shift of a hydrogen atom is called a 1, 2-hydride shift (or a 1,2-H shift).

Hydride ion = H:-. In the following example the migrating hydrogen atom and the associated electron pair



- Of these two rearrangement examples, hydride shift leads to a tertiary carbocation whereas alkyl shift leads to a secondary carbocation. Because a tertiary carbocation is more stable thana secondary carbocation, the hydride shift is favored in preference to the alkyl shift.

- Any C–H or C–C bond adjacent to a carbocation may shift (including C–C bonds that are part ofa ring), but only C–C and C–H bonds can migrate during carbocation rearrangement.
- The most common carbocation rearrangements involve a carbocation rearranging into a more stable carbocation, such as $2^o \rightarrow 3^o$ with resonance. (So use these rearrangements with

impunity)

- Rearrangements that transform a carbocation into another of apparently equal stability are less common, but they do occur.
- Rearrangement to a less stable carbocation is very unusual, but also does occur.

5 MARKS QUESTIONS

1. Explain Saytzeff's rule and its orientation
2. Explain in detail about rearrangement of carbocations

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