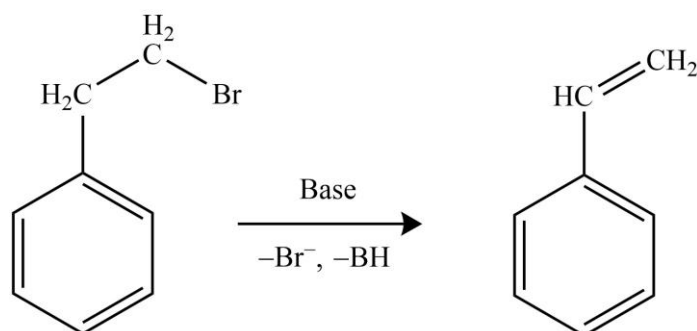


❖ Orientation of the Double Bond

In this section, we will discuss the effect of the orientation of the double bond (regio- and stereochemistry) on the reactivity of the elimination reaction.

➤ Regiochemistry of the Double Bond

The possibility of regioselectivity in elimination reactions arises if more than one carbon have β -hydrogens. For instance, the sec-butyl halide (two types of β -hydrogen) can result in either 1- or 2-butene whereas $\text{PhCH}_2\text{CH}_2\text{Br}$ is not able to do so (only $\text{PhCH}=\text{CH}_2$).

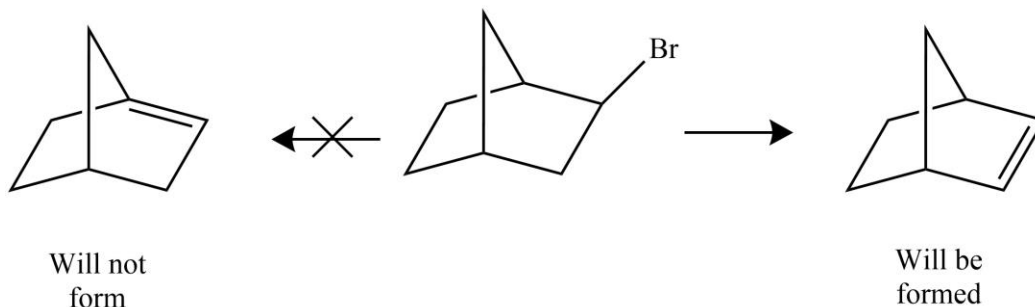


Therefore, the rules that dictate the major-minor products must be discussed for any stereochemical rationalization first.

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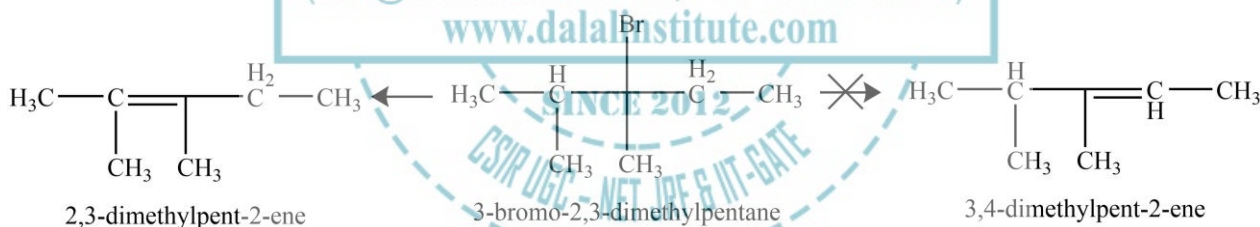
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Rule 1: The double bond will not shift to a bridgehead carbon irrespective of the mechanism-type until the ring size becomes quite big. This rule is also known as Bredt's rule because it was given Julius Bredt in 1902, and codification was completed in 1924.



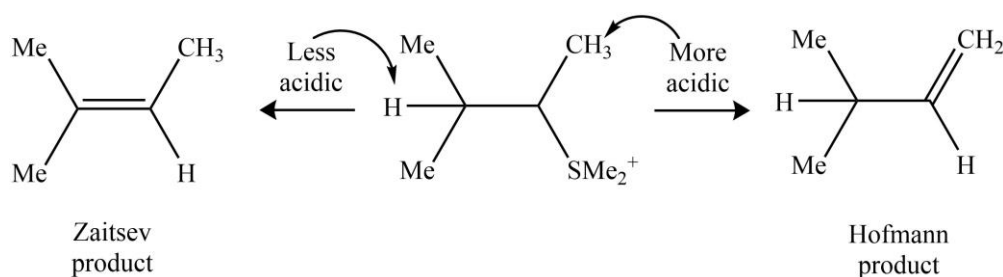
Rule 2: If there is a possibility of a newly formed double bond to get into conjugation with some previously present multiple bond or aromatic ring, it will always do so even if it leads to unfavorable stereochemistry.

Rule 3: The directional shift of the double bond in E_1 reactions is always decided by the relative stabilities of resulting products; which is because the initial departure of the leaving group leaves both possibilities open. In other words, the double bond moves primarily toward the more substituted carbon (Zaitsev's rule); which can be explained on the basis of the heat of hydration or hyper-conjugative structure. For instance, 2,3-dimethyl-2-pentene is formed from 3-bromo-2,3-dimethylpentane rather than either 3,4-dimethyl-2-pentene or 2-ethyl-3-methyl-1-butene.



Since the departure of the leaving group occurs first, the Zaitsev's rule dictates the orientation of double bond in E_1 reaction irrespective of the leaving group's nature (neutral or positive); however, in case it cannot be said for E_2 reactions, where the orientation of the double bond and the departure of the leaving group takes place simultaneously. Nevertheless, the non-Zaitsev product can also be the major product even in the case of E_1 eliminations because of reduced steric hindrance, or the formation of ion-pair.

Rule 4: It is quite a well-known fact that a trans β proton is required for the anti E_2 mechanism to be active; which is accessible only in one direction creating only one double-bond-shifting possibility. However, it is limited to the cyclic systems because the molecule may free rotation about carbon-carbon single bond (if the steric hindrance isn't very high). On the other hand, if two or more carbons have trans- β hydrogens, two types of products can be obtained; sometimes Zaitsev's product (double bond shifting toward the more substituted carbon), sometimes Hofmann's product (double bond shifting toward the least substituted carbon).



It has also been observed that Zaitsev's rule is followed in all substrates if the compound has uncharged nucleofuges (leaving as negative ions like Cl^-); whereas Hofmann's rule is followed if the compound has charged nucleofuges (leaving as neutral ions like NR_3^+) provided that the substrate is acyclic, otherwise Zaitsev's product (i.e., if the leaving group is connected to a benzene ring). Now because Zaitsev's rule gives rise to the thermodynamically stable product, its outranking by Hofmann's rule in some compounds should also be explained. This change of double bond orientation in acyclic systems can be rationalized in the terms of two different factors.



The first one is that the β -hydrogen becomes less acidic due to the presence of the alkyl group, which in turn favors Hoffman's rule. The second one is the fact that positively charged groups are generally larger in size than the neutral group, and therefore a CH_3 group (less substituted) is more prone to attack than a primary or secondary carbon; in other words, steric effects dictate the final product.

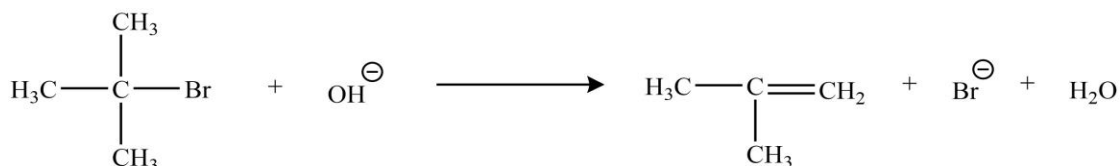
Rule 5: It has been observed that the Hofmann orientation is significantly favored over the Zaitsev product in syn- E_2 eliminations.

Rule 6: The regioselectivity is of less importance as far as the E_1CB -type reactions are concerned because this pathway is typically found in the systems with an electron-withdrawing group at β -site, attracting double bond movement towards itself.

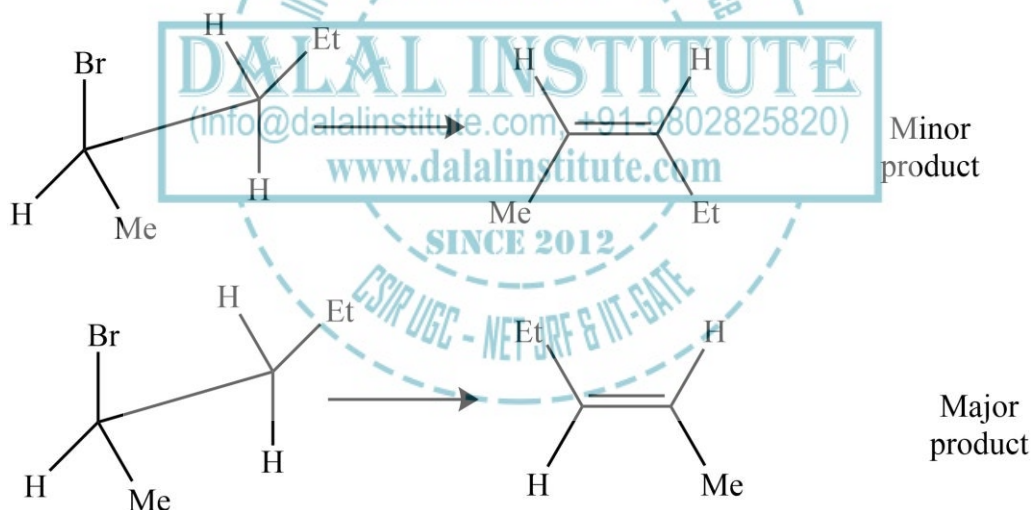
Rule 7: It is a well-known fact that E_2C reactions are susceptible to Zaitsev orientation, and this preference is of great importance as far as commercial production is concerned. However, the non-Zaitsev product is also obtained in some cases where conjugation with the aromatic ring is obtainable.

➤ **Stereochemistry of the Double Bond**

If CHAB–CGGX or CH₃–CABX type compounds undergo elimination, the resulting alkene cannot show cis-, trans-isomers. However, the CH₂E–CABX CHEG–CABX type compounds do have the ability to give rise to cis- and trans- isomers after undergoing elimination. For instance, consider the following transformation.



It has been observed that the threo- and erythro-compound gives rise to trans- and cis- alkene; respectively. Furthermore, two conformations can be obtained for the transition state in the case of compound II, where two isomers can be synthesized. Nevertheless, the eclipsing effects will dictate the major-minor one; like the Zaitsev elimination of 2-bromopentane leads to the trans-isomer as major. This because confirmation A (Et is in between H and Br) is more stable than conformation B (Et is in between Me and Br), and the effect becomes more dominating as the groups get bigger.



Moreover, the ratio of cis/trans isomers in the anti-E₂ reaction is also dictated by the solvent, nature of the leaving group, the substrate, and the attacking base. The complete picture of these effects is still not clear as far as the stereochemistry of the double bond is concerned. For instance, E₁-system with a bigger D-E pair opposite to the smaller AB pair is more stable if the carbocation free to rotate; and therefore, we should get the corresponding alkene. On the other hand, E₂-like products will be formed if the carbocation formed is not totally free; and the same is true for E₁CB reactions.

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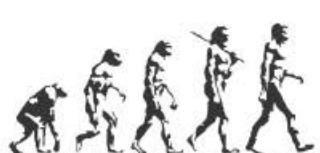
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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