

# Elimination Reactions:

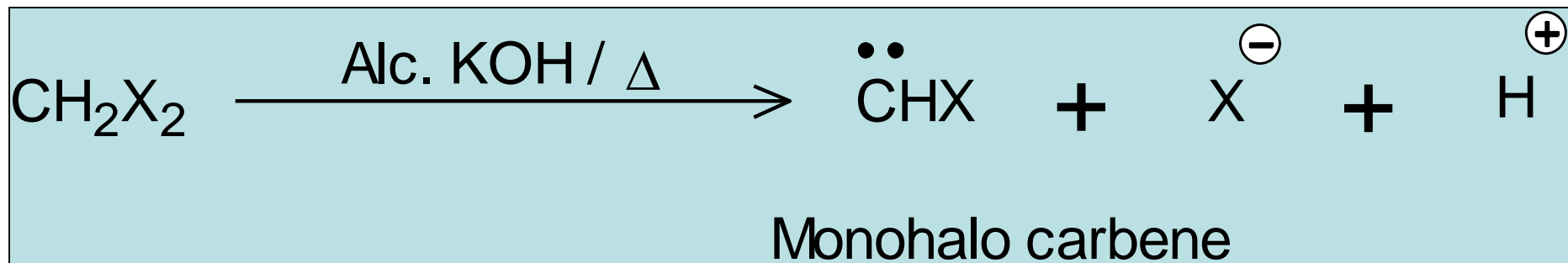
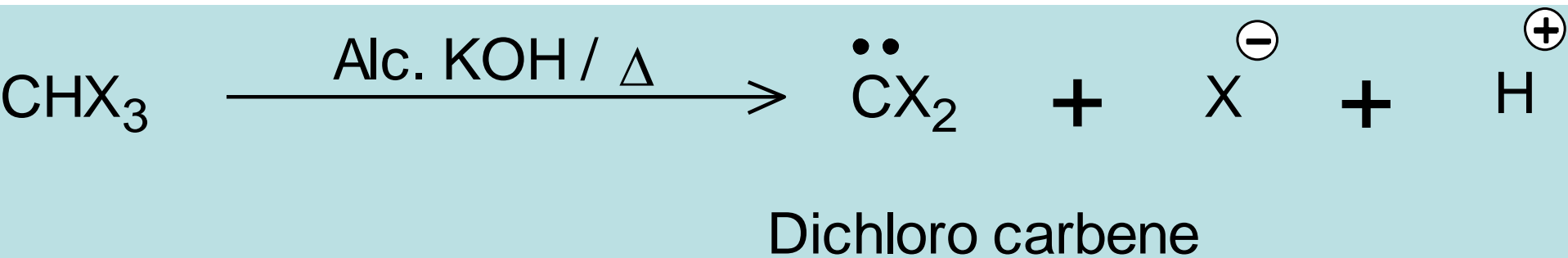
These are just reverse of addition reactions. These involve the removal of atoms or group of atoms from a molecule. Elimination reactions are generally endothermic and take place on heating.

Elimination reactions are classified into two categories.

$\alpha$ -Elimination reactions or 1,1-elimination reactions

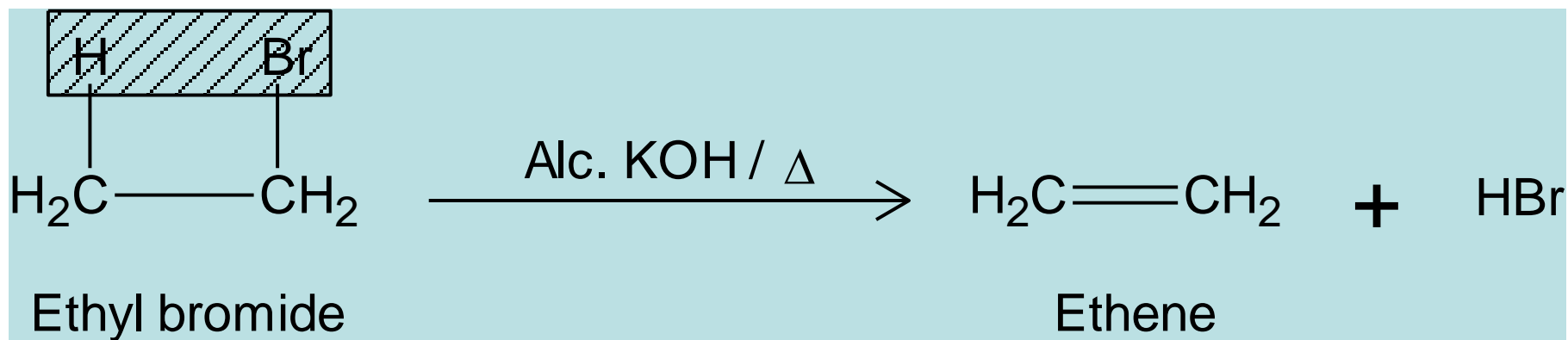
$\beta$ -Elimination reactions or 1,2-elimination reactions

- **(i)  $\alpha$ -Elimination reactions:** Those elimination reactions in which both the atoms or groups are removed from the same carbon atom of the molecule. This reaction is mainly given by gem. di or trihalides having at least one  $\alpha$ -H atom. Products of these reactions are halocarbenes.



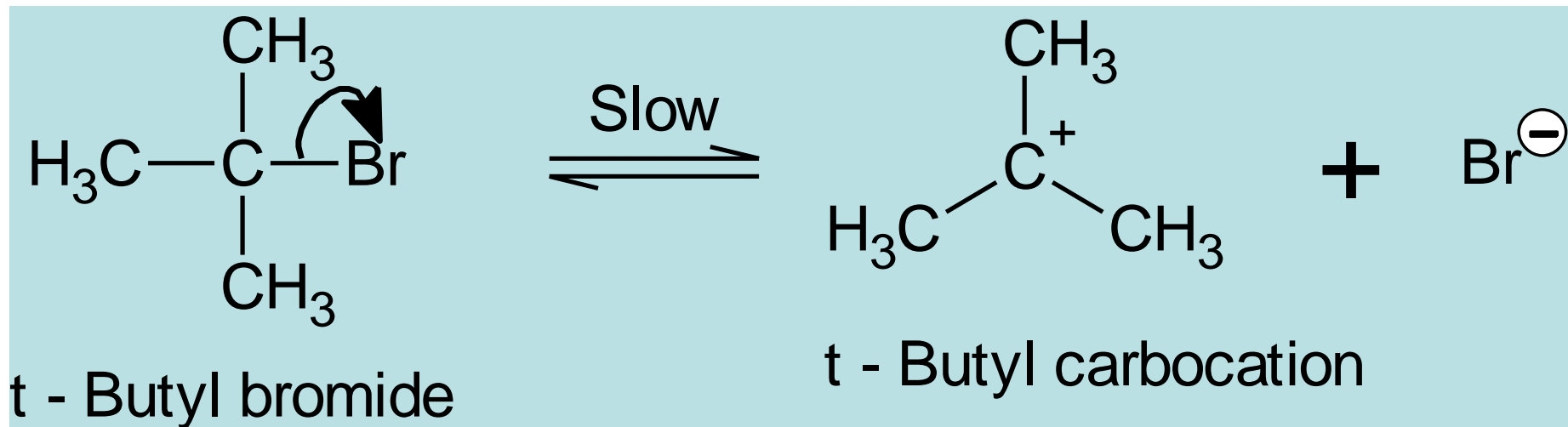
- **(ii)  $\beta$ -Elimination reactions:** Those elimination reactions in which removal of functional group (leaving group) from  $\alpha$ -carbon atom and other group (generally H-atom) from  $\beta$ -C-atom take place are called  $\beta$ -elimination reactions. In this reaction there is loss of two  $\sigma$  bonds and gain of one  $\pi$  bond.
- $\beta$ -Elimination reactions are divided into following types.
  - $E^1$  (Elimination unimolecular)
  - $E^2$  (Elimination bimolecular)
  - $E^1cB$  (Elimination unimolecular conjugate base)

- **Examples of elimination reactions:**  
**Dehydrohalogenation:** Removal of hydrogen halide from a molecule is known as dehydrohalogenation.
- Example: Dehydrohalogenation of alkyl halides in presence of alcoholic KOH.

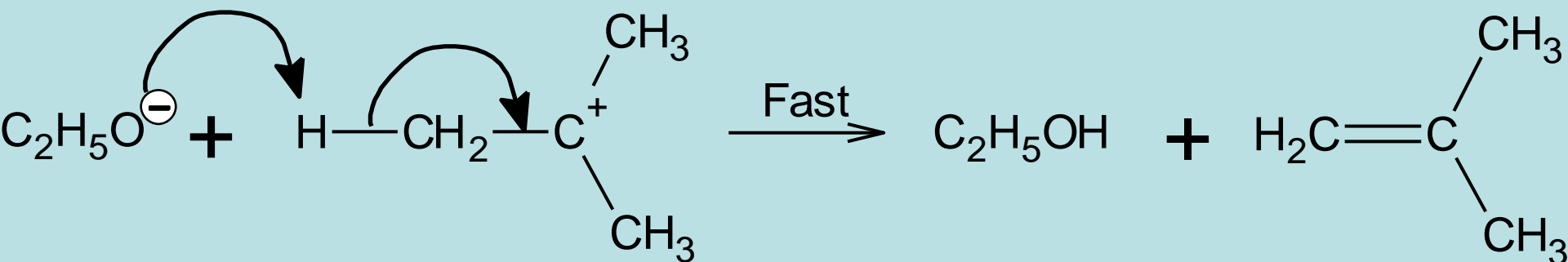




- The mechanism of the reaction involves the two steps.
- The first step involves the slow ionization of bromide to form carbocation.



- The second step is fast step and involves the removal of H atom by base from carbocation to form the final product.



From the kinetic studies it is found that the rate of this reaction depends only upon the concentration of alkyl halide and independent of conc. of the base.

Rate  $\propto$   $[(\text{CH}_3)_3\text{C Br}]$

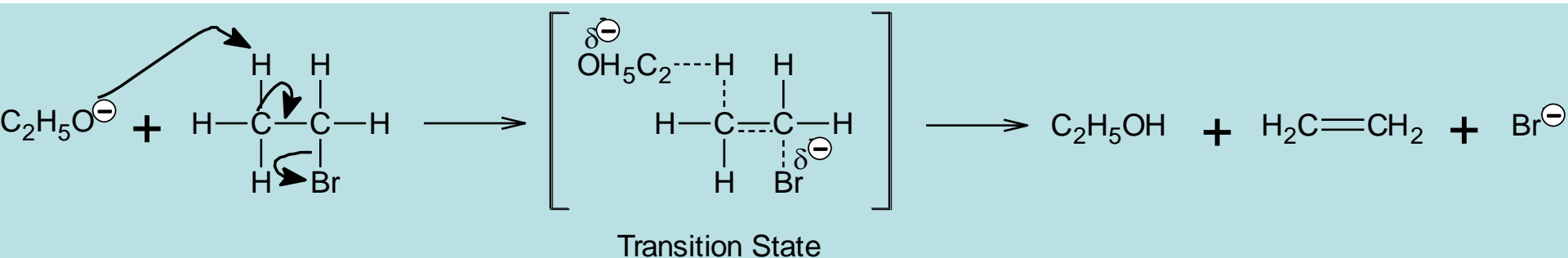
Rate =  $k[(\text{CH}_3)_3\text{C Br}]$ .....Unimolecular reaction

- **E<sup>2</sup> mechanism:** E<sup>2</sup> stands for elimination bimolecular.
- Consider the reaction between primary alkyl halide such as ethyl bromide and alcoholic KOH to form alkene (ethene).

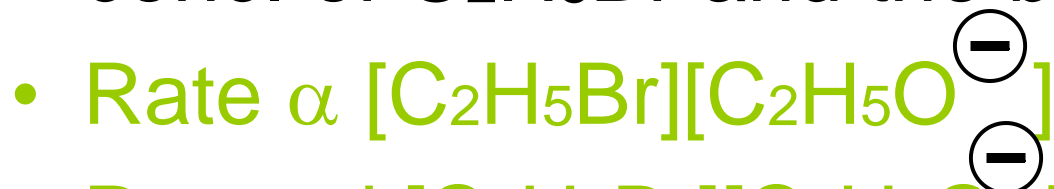




- The mechanism of this reaction is single step and involves the formation of transition state. Thus  $E^2$  reactions are concerted reactions.
- In  $E^2$  reactions, both the leaving groups should be antiperiplanar i.e., both leaving groups should be in the same plane but should have anti configuration (i.e., angle is  $180^\circ$ ).



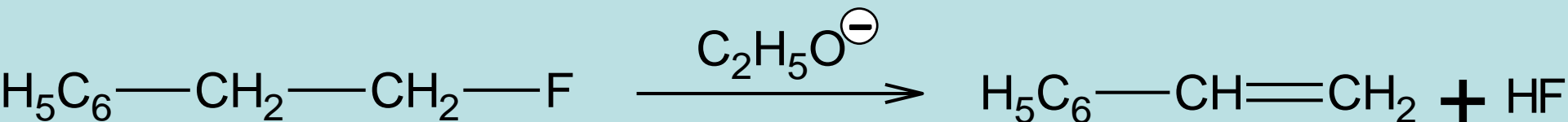
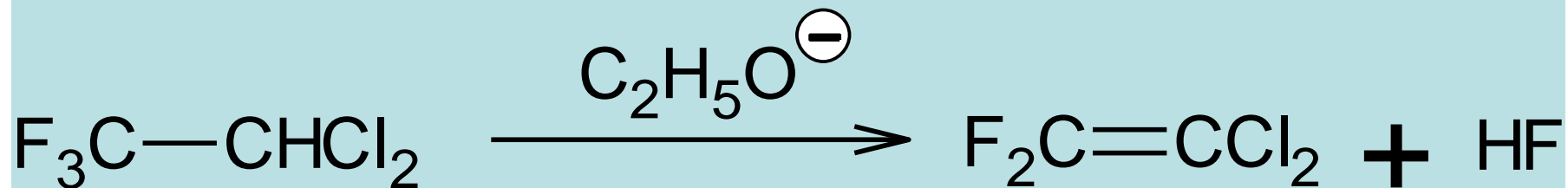
- From kinetic studies it has been found that rate of this reaction depends both upon conc. of C<sub>2</sub>H<sub>5</sub>Br and the base.



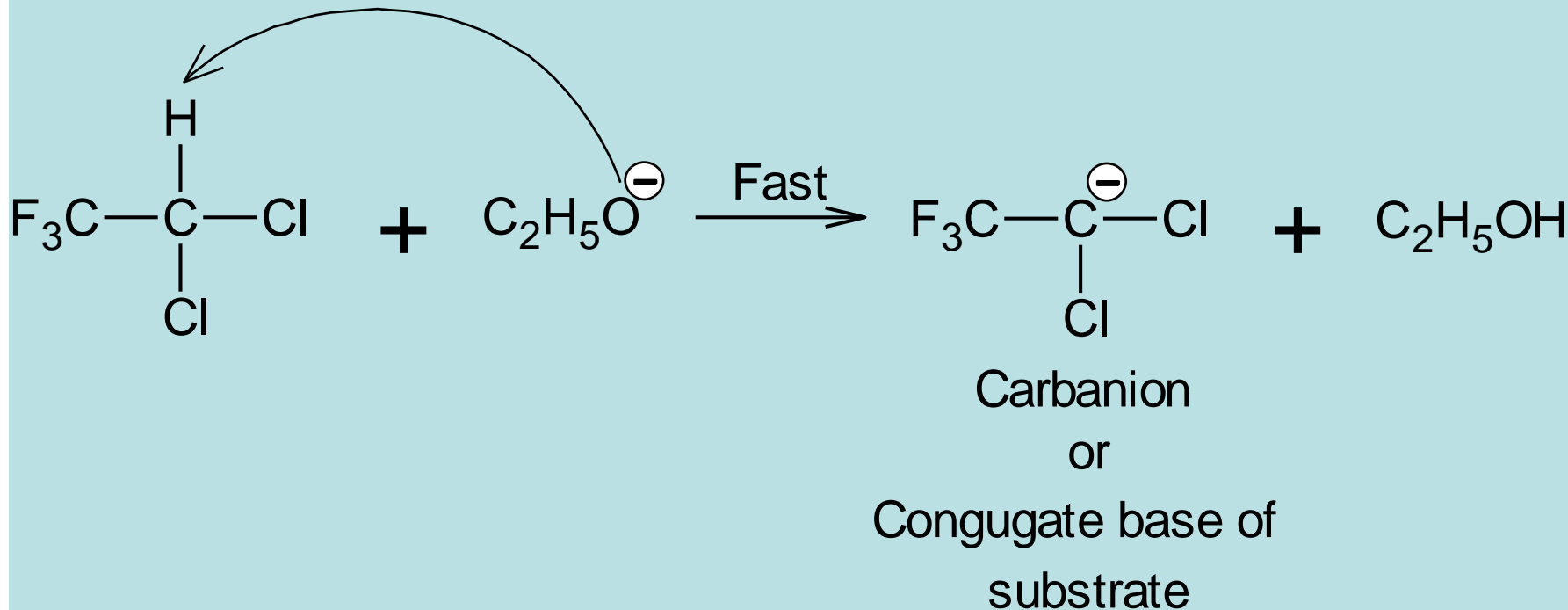
..... bimolecular reaction

- **E<sup>1</sup>cB mechanism:** E<sup>1</sup>cB stands for elimination unimolecular conjugate base.
- It is two steps process and involved the formation of conjugate base (carbanion) of the reactant. Thus E<sup>1</sup>cB mechanism is limited to substrates which can be stabilize the carbanion as reaction intermediate by resonance or by -I effect. In this type of mechanism the β-hydrogen atom of the reactant should be highly acidic so that it can be easily removed as proton to give carbanion.

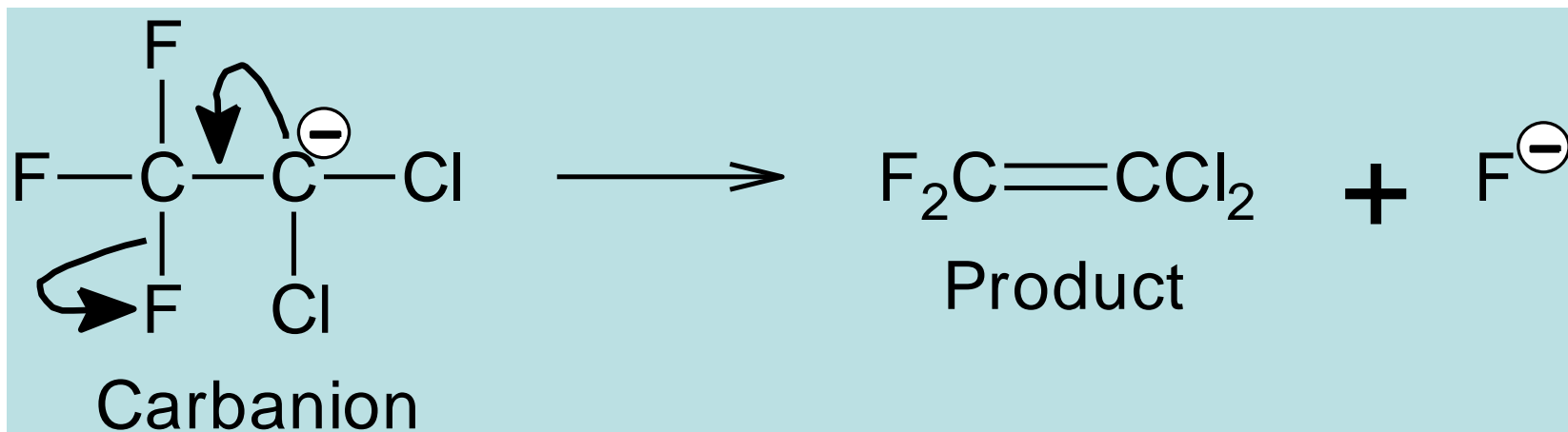
- **Examples:**



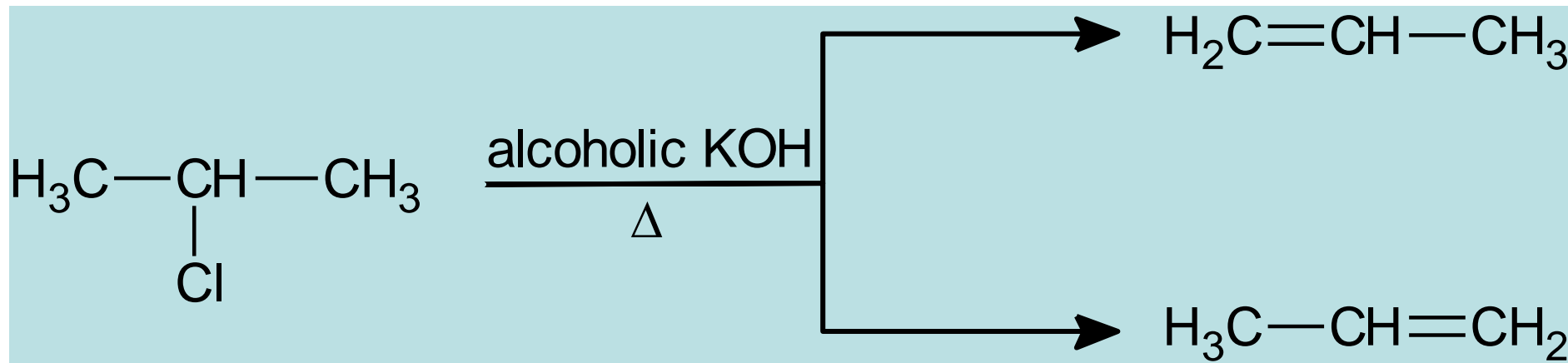
This process of elimination involves two steps like  $\text{E}^1$  mechanism. In  $\text{E}^1$  mechanism, X leaves first followed by H. In the  $\text{E}^1\text{cB}$  mechanism, the H leaves first and then the X. This mechanism thus involves a carbanion intermediate as follows:



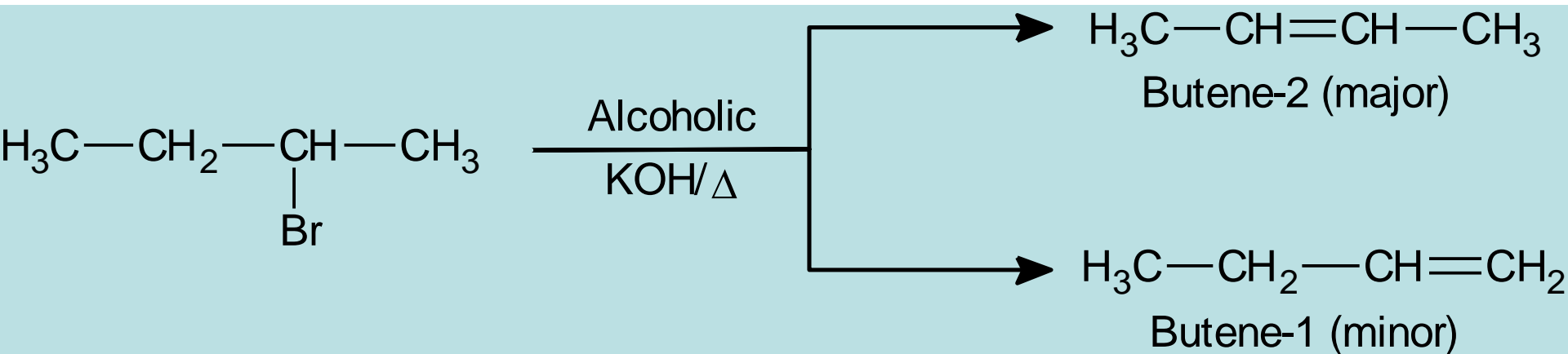
The carbanion so formed is stabilized by  $-I$  effect of  $\text{CF}_3$  &  $\text{Cl}$  atoms.



- Orientation in elimination reactions:** It is found that elimination in a symmetrical organic halide gives rise to a single alkene. e.g., 2-chloropropane forms only one product; propene.

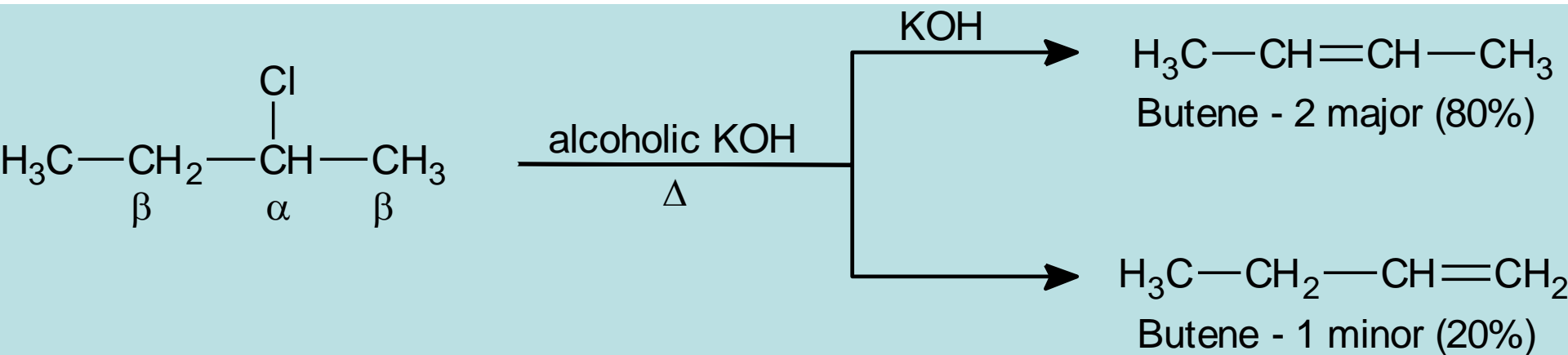


- But in an unsymmetrical alkyl halide, elimination may proceed in more than one direction and a mixture of isomeric alkenes results. e.g., 2-Bromobutane forms two products.



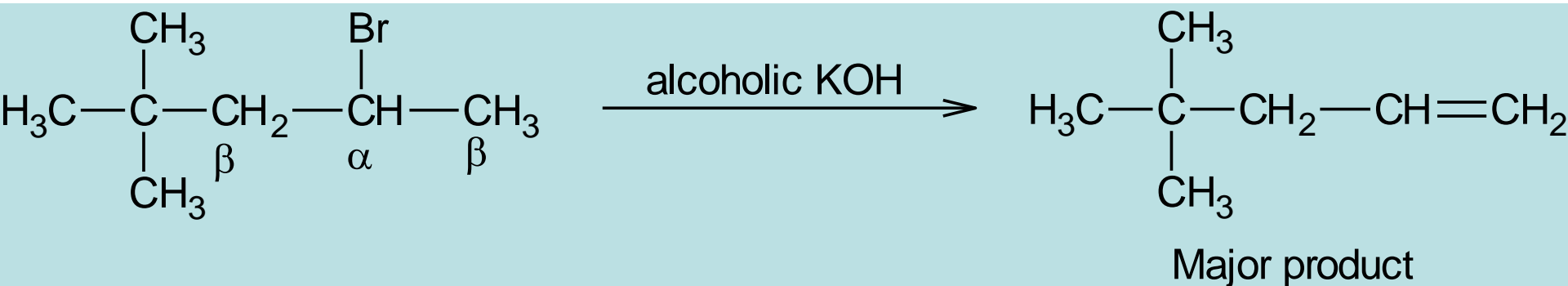
Thus, if the substrate is unsymmetrical then there will be more than one product. The major product of the reaction can be known by two empirical rules.

- **1. Saytzeff rule** : According to this rule, major product is the most substituted alkene i.e., major product is obtained by elimination of H-atom from that  $\beta$ -carbon atom which has the least number of H-atoms or that  $\beta$ -carbon atom which is most substituted and the product is called **Saytzeff product**.

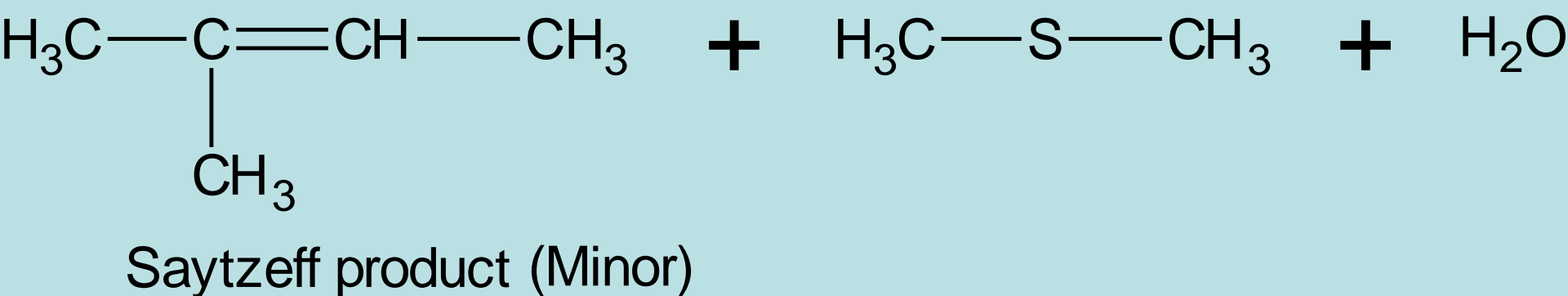
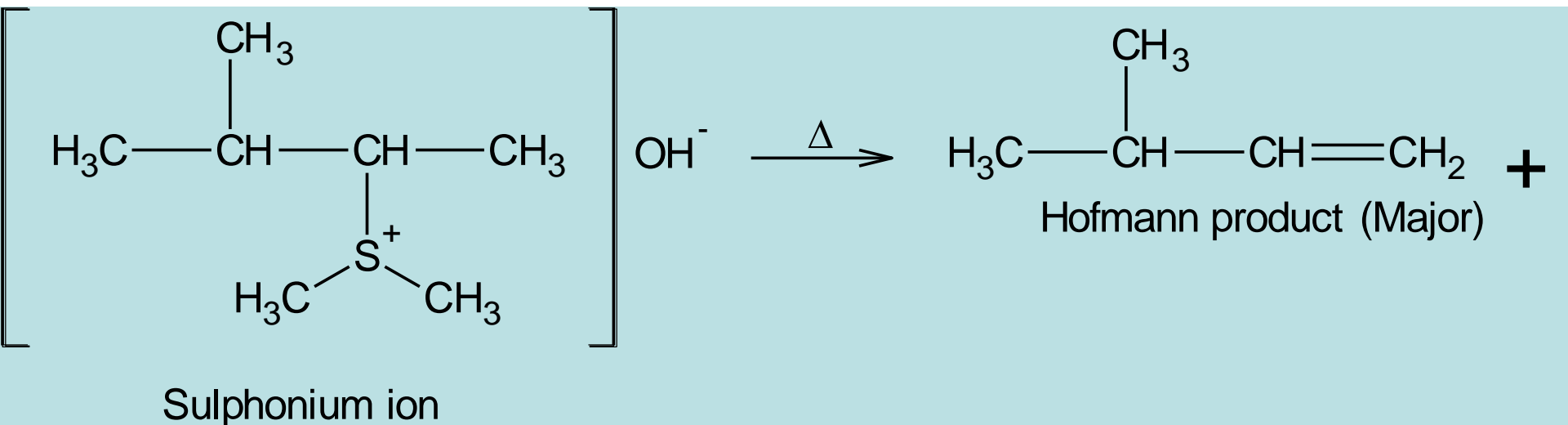
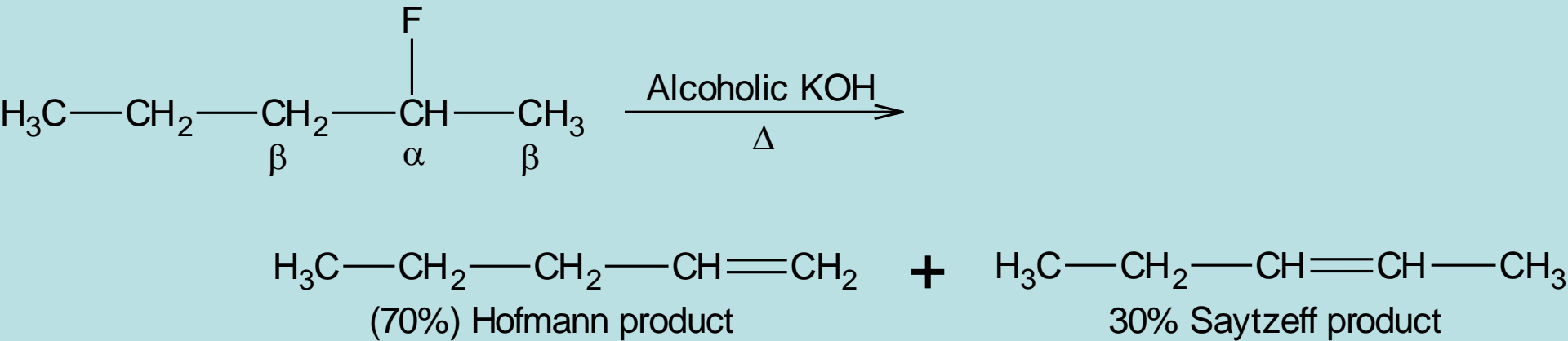


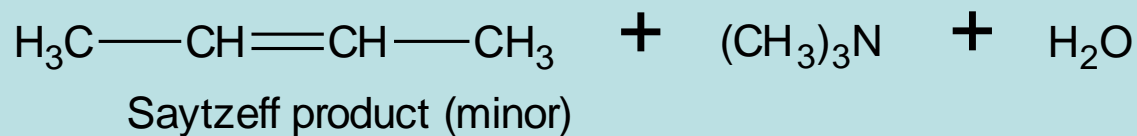
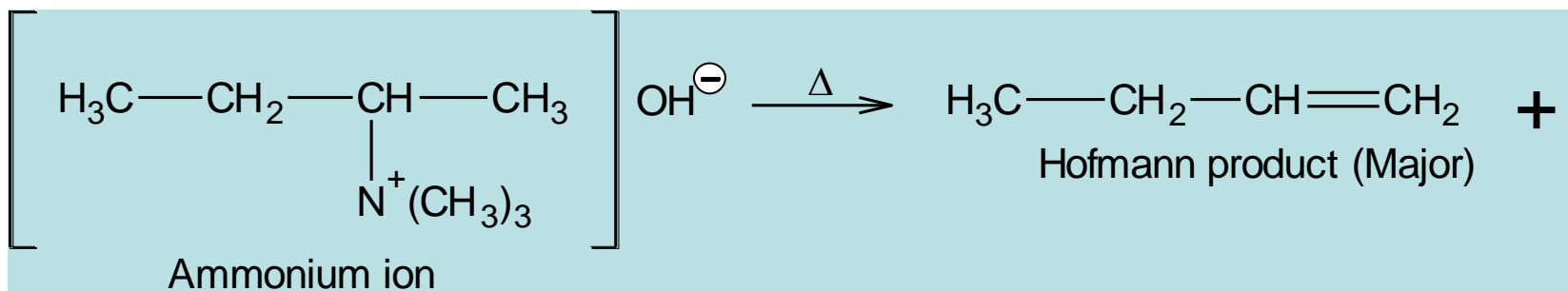


- **2. Hofmann rule:** According to this rule the major product is always least substituted alkene i.e., major product is formed by elimination of H-atom from that  $\beta$ -carbon atom which has maximum number of H-atoms. i.e.,  $\beta$ -carbon atom which is least substituted. The product of the reaction is known as **Hofmann product**.

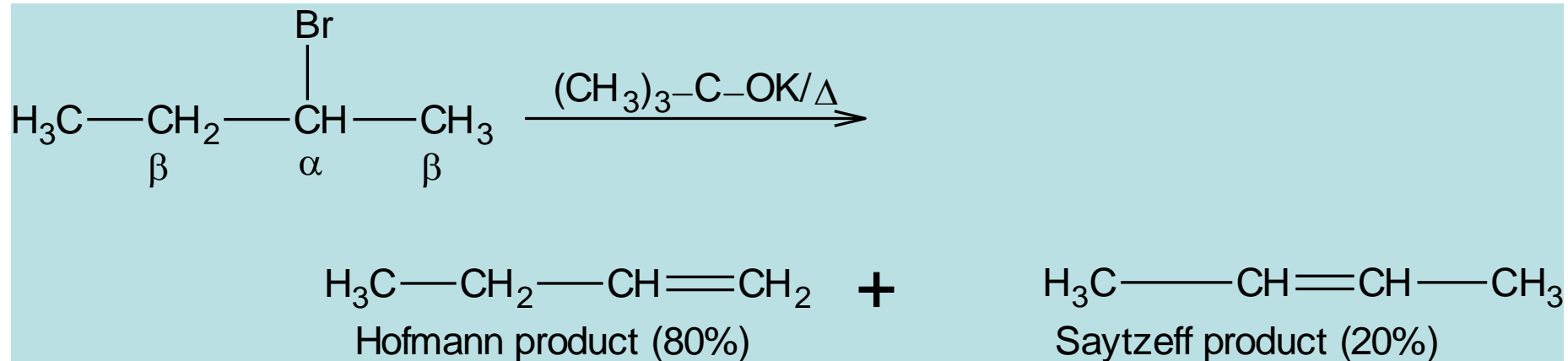


- **It is found that:**
- 1. In  $E^1$  reactions, the product formation always takes place by Saytzeff rule.
- 2. In  $E^1cB$  reactions, the product formation always takes place by Hofmann rule.
- 3. In  $E^2$  reactions, product formation takes place by Saytzeff as well as Hofmann rule. In almost all  $E^2$  reactions product formation takes place by Saytzeff rule. Only in following cases product formation takes place by Hofmann rule.
- (i) Dehydrohalogenation of alkyl halides when leaving group is very poor or bulky e.g.,

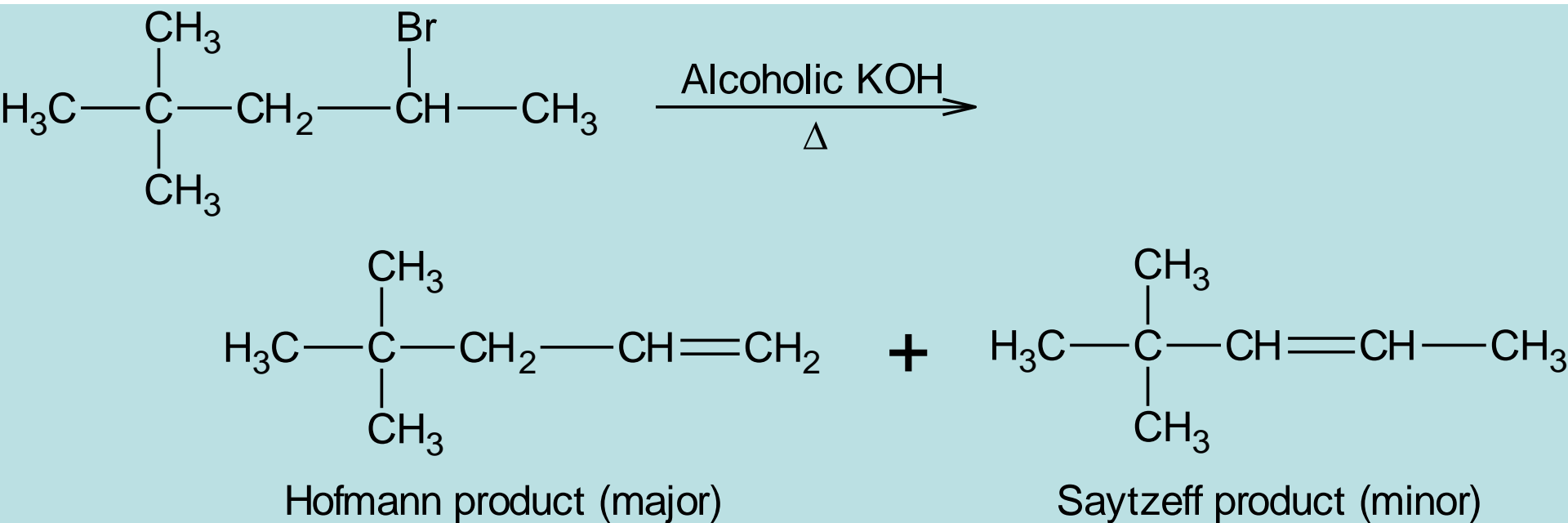




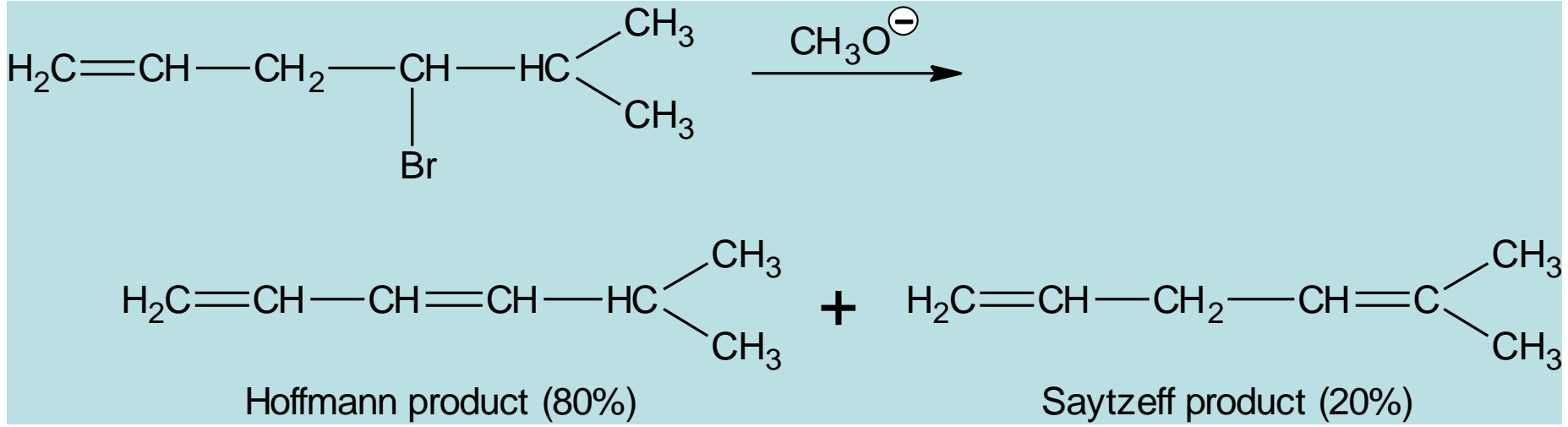
- (ii)  $1^\circ$  and  $2^\circ$  alkyl halides give Hofmann product when the size of the base is bulky e.g., Na or K salt of t-butoxide.



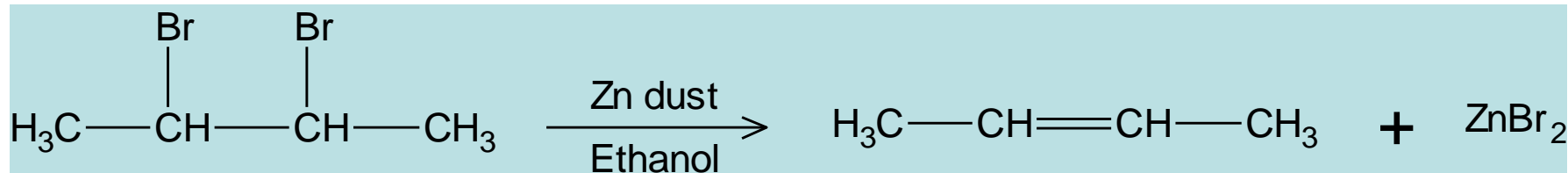
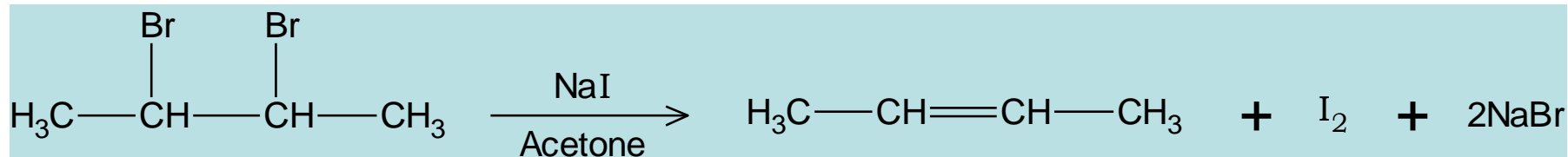
- (iii) 1° and 2° alkyl halides having quaternary  $\gamma$ -carbon give Hofmann product due to steric hindrance at  $\beta$ -carbon atom.



- (iv) When an alkyl halide contains one or more double bond.

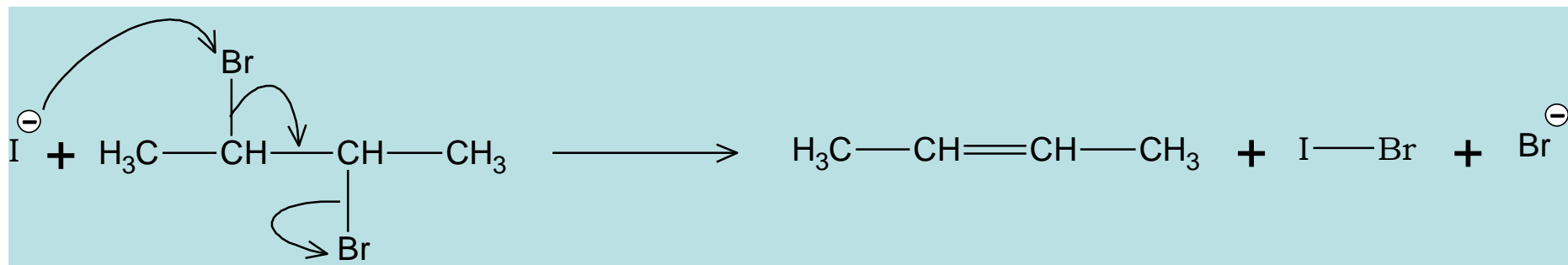


- Dehalogenation:** Removal of halogens from a molecule is known as dehalogenation. Vicinal dihalides undergo dehalogenation when they are heated with solution of NaI in acetone or with Zn dust and ethanol or Ag/ethanol.

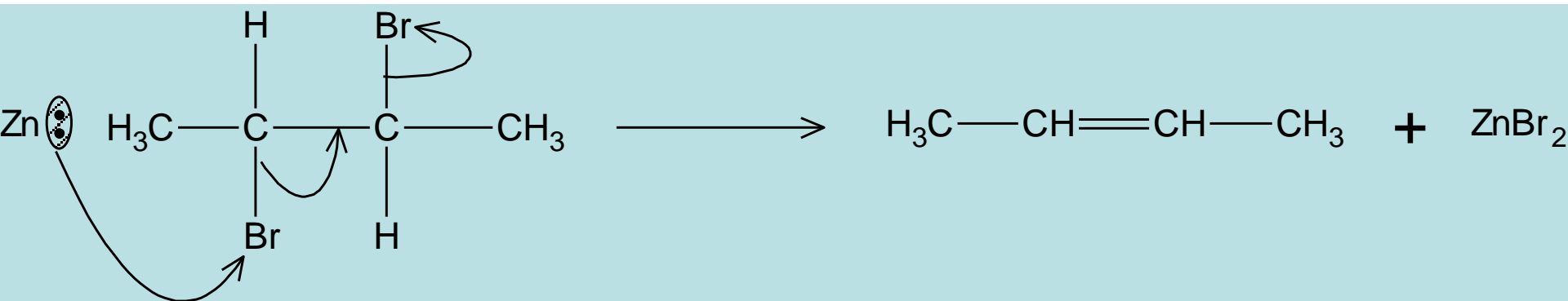




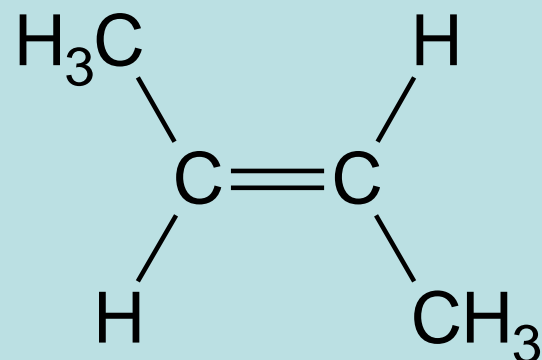
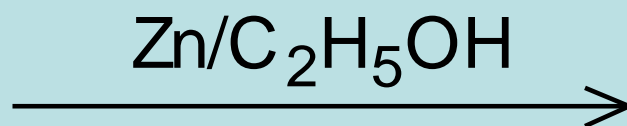
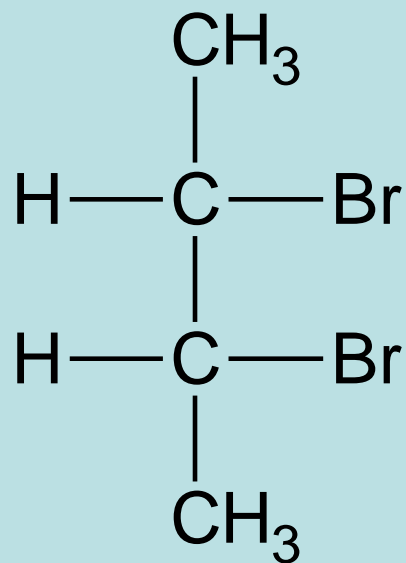
- Dehalogenation by NaI takes place by an E<sup>2</sup> mechanism as follows:



- Dehalogenation by Zn or Ag also takes place by E<sup>2</sup> mechanism as follows:

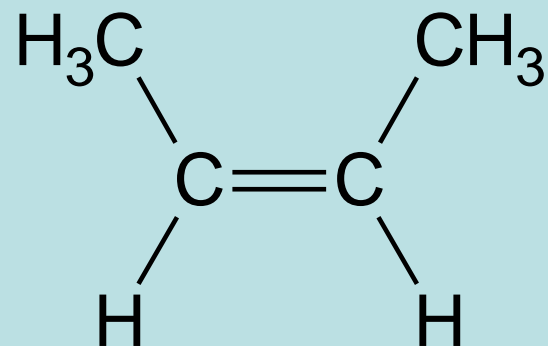
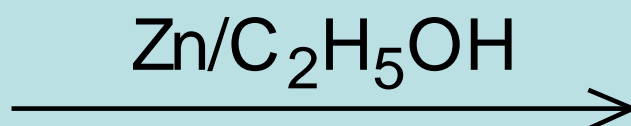
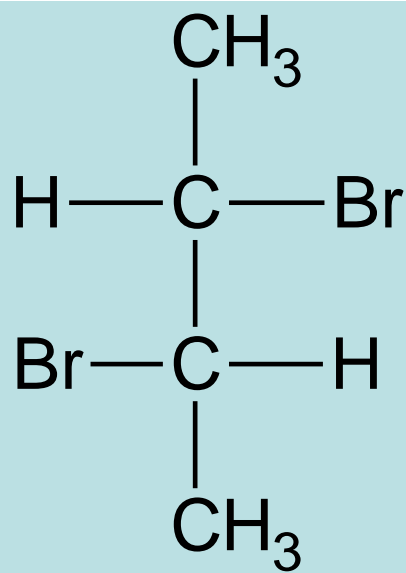


- **Stereochemistry of dehalogenation reactions:**  
Dehalogenation reactions are anti elimination reactions. These reactions are also stereoselective as well as stereospecific. Geometry of alkene formed during dehalogenation reaction depends on the configuration of the  $\alpha$ ,  $\beta$ -dihalo alkanes in which  $\alpha$  and  $\beta$  carbons are chiral. On dehalogenation:
  - Meso form gives trans alkene.
  - (+) or (-) form gives cis alkene.



Meso-2, 3-dibromo butane

trans-2-Butene



(+) or (-) form

cis-2-Butene

- **Dehydration:** Removal of water from a molecule is known as dehydration. Dehydrating agents for alcohols are conc.  $\text{H}_2\text{SO}_4/\Delta$ ,  $\text{KHSO}_4/\Delta$ ,  $\text{H}_3\text{PO}_4/\Delta$ , anhydrous  $\text{Al}_2\text{O}_3/\Delta$ , anhydrous  $\text{PCl}_5/\Delta$ , anhydrous  $\text{ZnCl}_2/\Delta$ ,  $\text{BF}_3/\Delta$  and  $\text{P}_2\text{O}_5/\Delta$ .
- The decreasing order of reactivity of alcohols for dehydration is as follows:
- $3^\circ$  alcohol  $>$   $2^\circ$  alcohol  $>$   $1^\circ$  alcohol

