Alkenes
2 - Elimination Reactions

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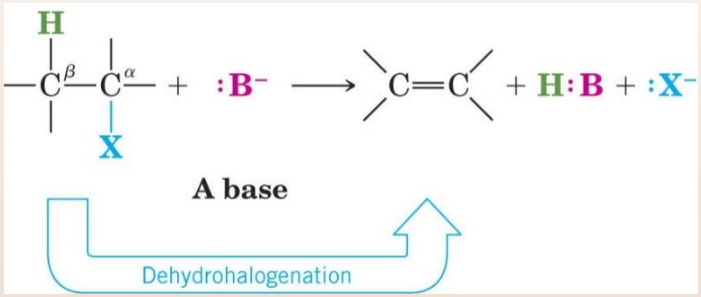
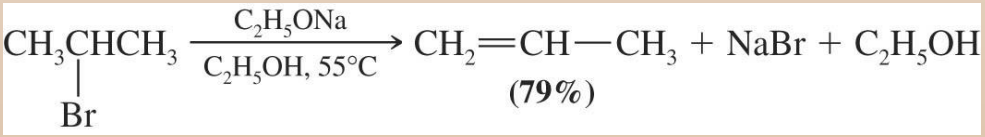
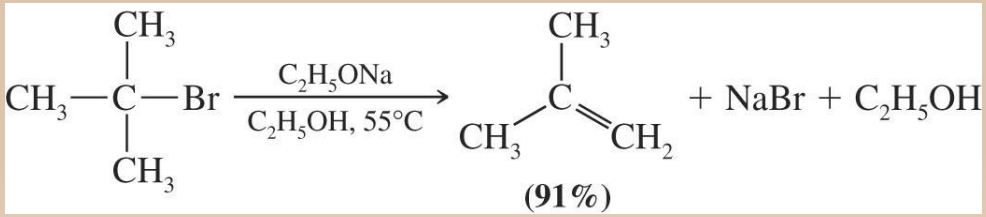
Elimination Reaction



- There are two mechanisms for elimination. E1 and E2.
- Product of this reaction is an alkene
- Elimination is called α β-elimination (α carbon is the one that has the leaving group and β is the one next to it.) It can also be 1,2-elimination. 1 is the carbon with the LG.





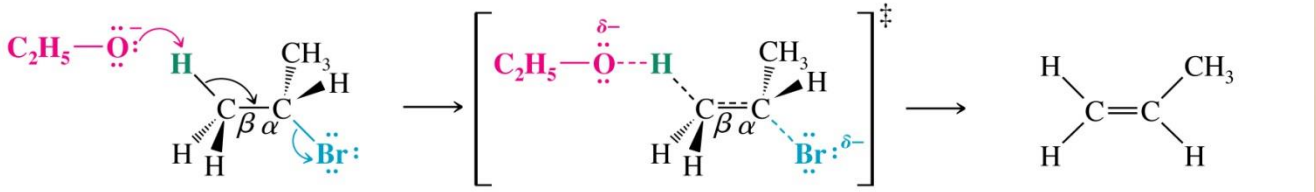
E2 Mechanism

- Bimolecular elimination
- Requires a strong base
- Halide leaving and proton abstraction happens simultaneously - no intermediate.

Reaction:

$$C_2H_5O^- + CH_3CHBrCH_3 \longrightarrow CH_2{=}CHCH_3 + C_2H_5OH + Br^-$$

Mechanism:



The basic ethoxide ion begins to remove a proton from the β carbon using its electron pair to form a bond to it. At the same time, the electron pair of the β C—H bond begins to move in to become the π bond of a double bond, and the bromine begins to depart with the electrons that bonded it to the α carbon

Transition state

Partial bonds in the transition state extend from the oxygen atom that is removing the β hydrogen, through the carbon skeleton of the developing double bond, to the departing leaving group. The flow of electron density is from the base toward the leaving group as an electron pair fills the π bonding orbital of the alkene.

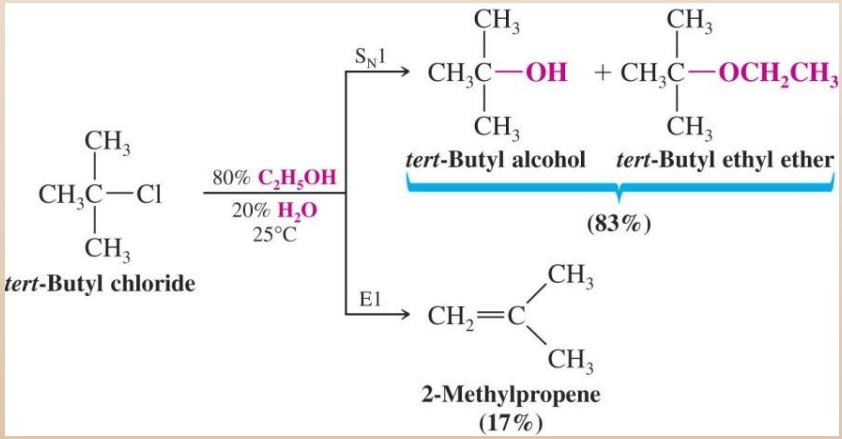
+

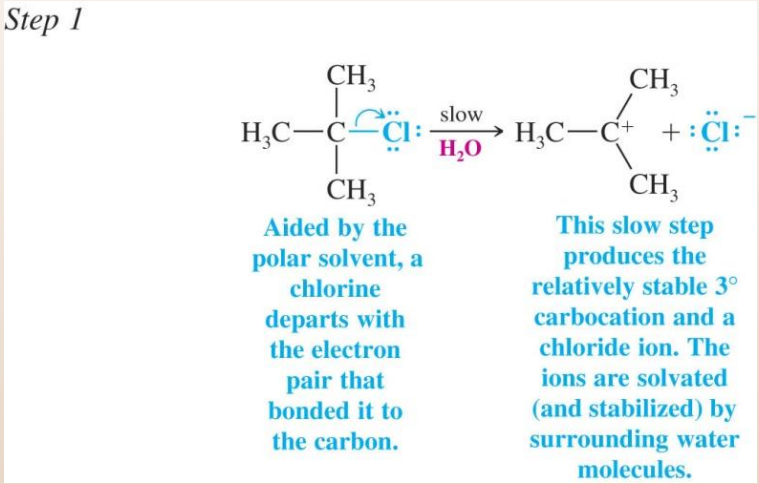
$C_2H_5—\ddot{O}H + :\ddot{Br}:^-$

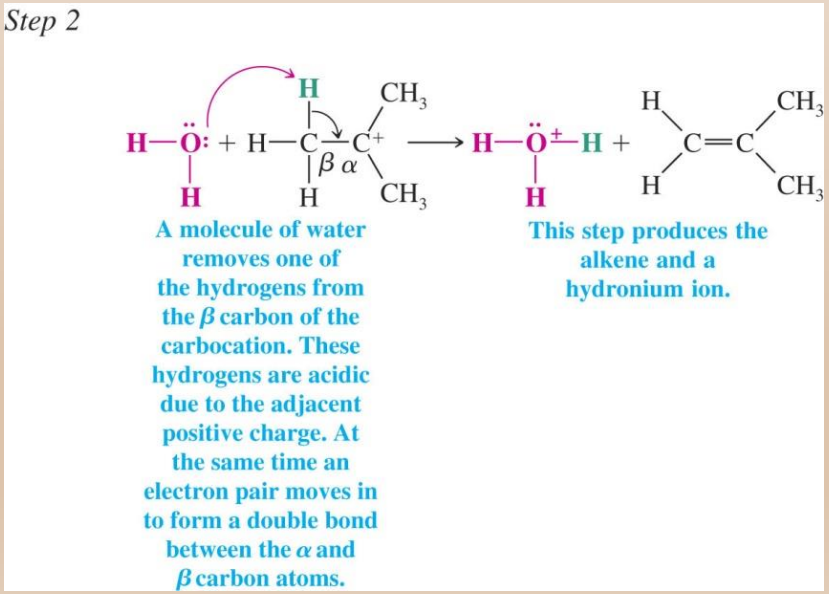
At completion of the reaction, the double bond is fully formed and the alkene has a trigonal planar geometry at each carbon atom. The other products are a molecule of ethanol and a bromide ion.

E1 Mechanism

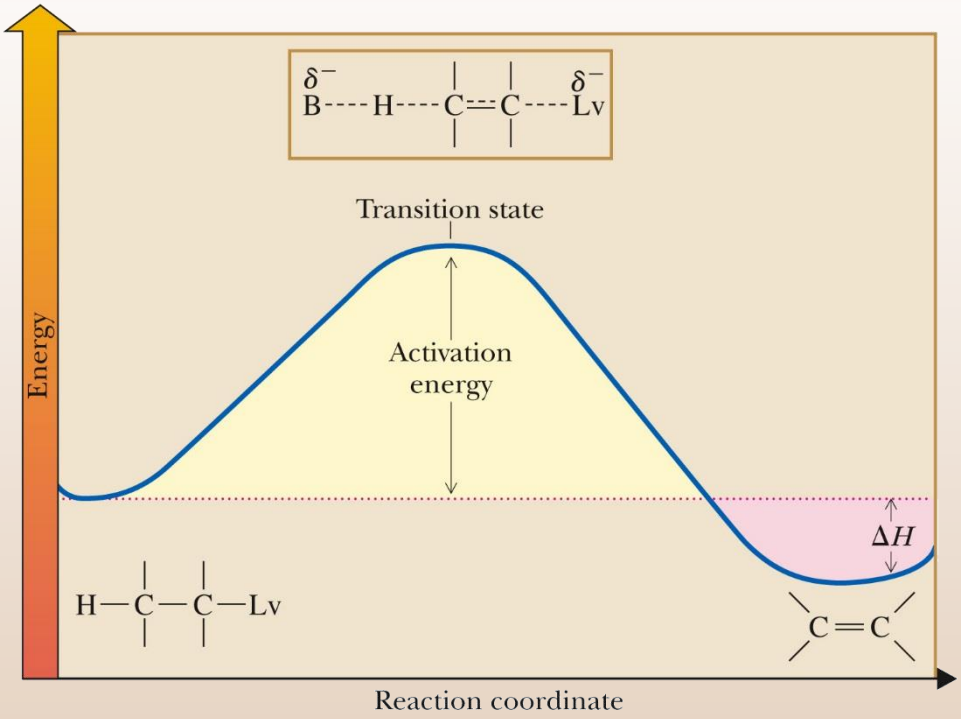
- Unimolecular elimination
- Two groups lost (usually X^- and H^+)
- Nucleophile will also be the base
- Also have S_N1 products (mixture)



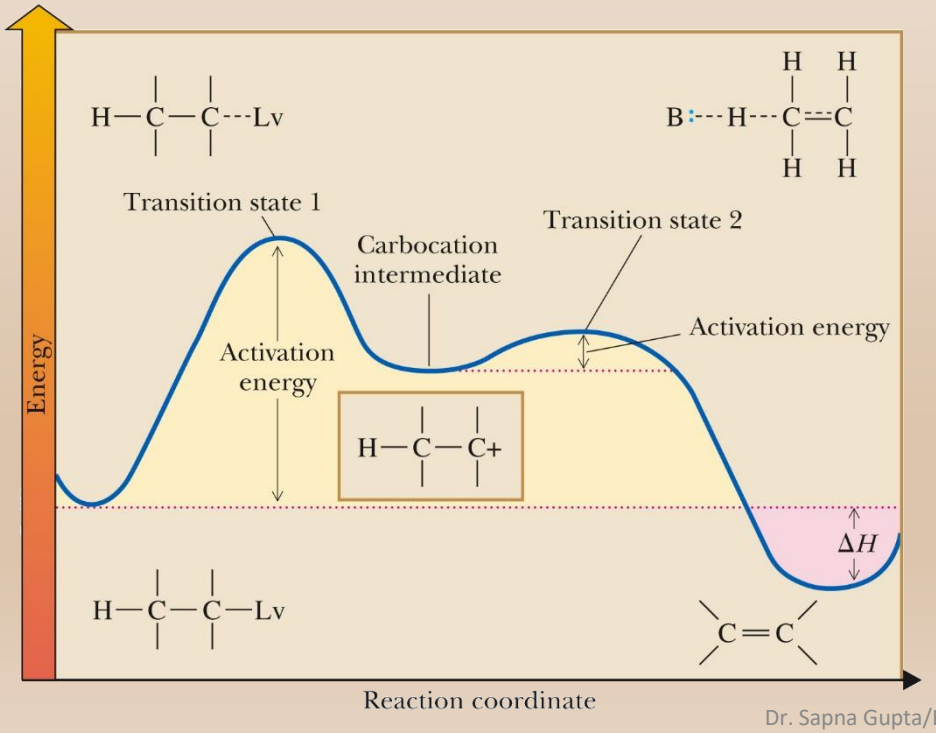




E2 Mechanism - Energy Diagram



E1 Mechanism – Energy Diagram

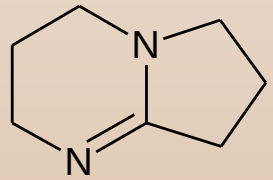


Bases

- Both E1 and E2 require good bases but E2 more than E1.
- Bases are used here as they have the ability to abstract protons.
- Good bases can also be good nucleophiles, so it can be challenging to decide whether to do E2 or S_N2 can be challenging.
- Some good bases are:

  H^-, DBN (1,5-Diazabiyclo[4.3.0]non-5-ene;

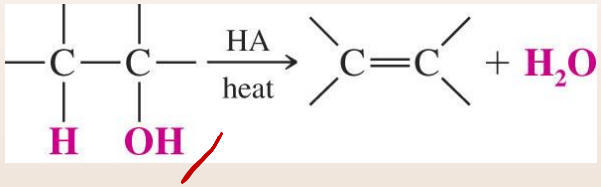
  structure shown on the side)

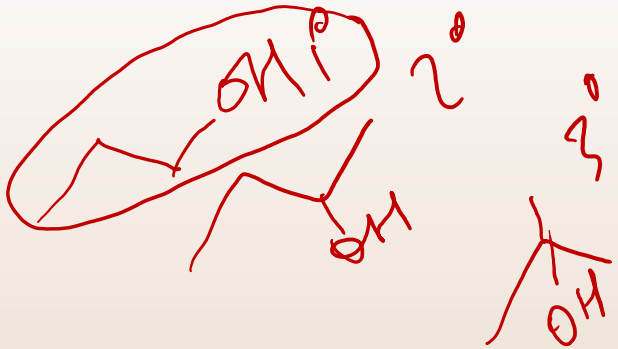


- Below are some oxides that are good Nu and bases:

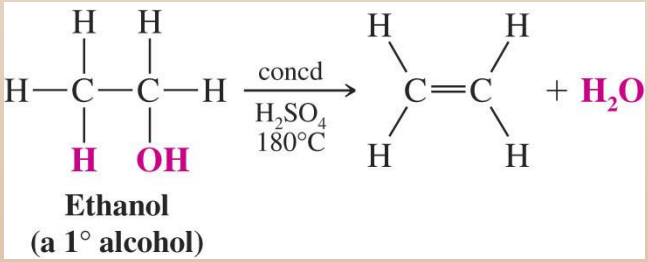
  OH^-, MeO^-, EtO^-, $tBuO^-$

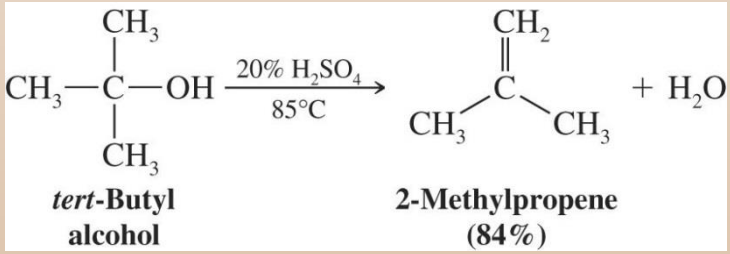
E1 - Dehydration of Alcohols





- Elimination is favored over substitution at higher temperatures
- Typical acids used in dehydration are sulfuric acid and phosphoric acid
- The temperature and concentration of acid required to dehydrate depends on the structure of the alcohol
  - Primary alcohols are most difficult to dehydrate, tertiary are the easiest

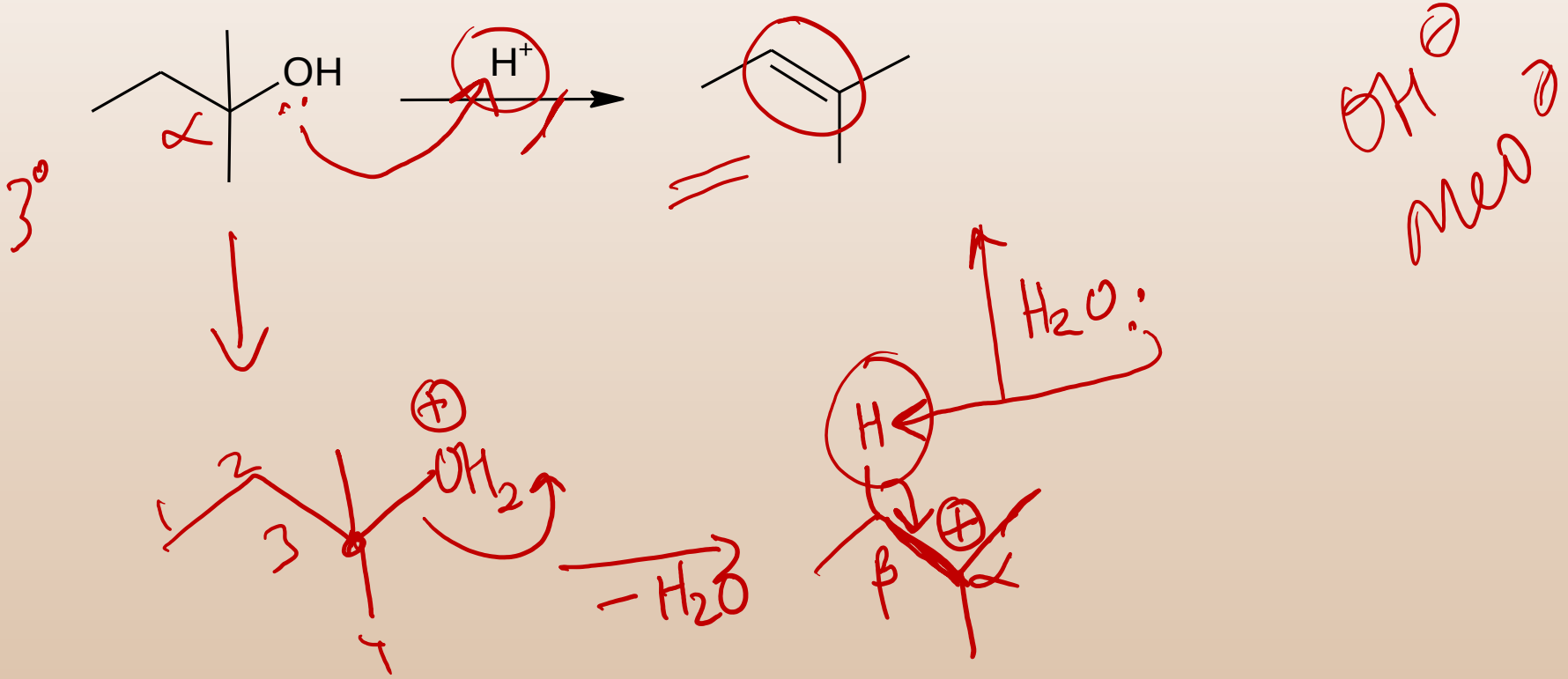




- Rearrangements of the carbon skeleton can occur

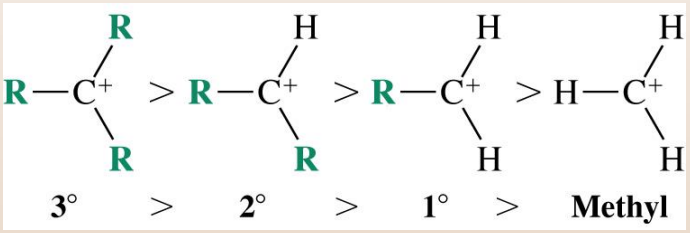
Mechanism of Dehydration

- E1 mechanism; the acid is a catalyst and needed only in small quantity



Carbocation Stability in Dehydration

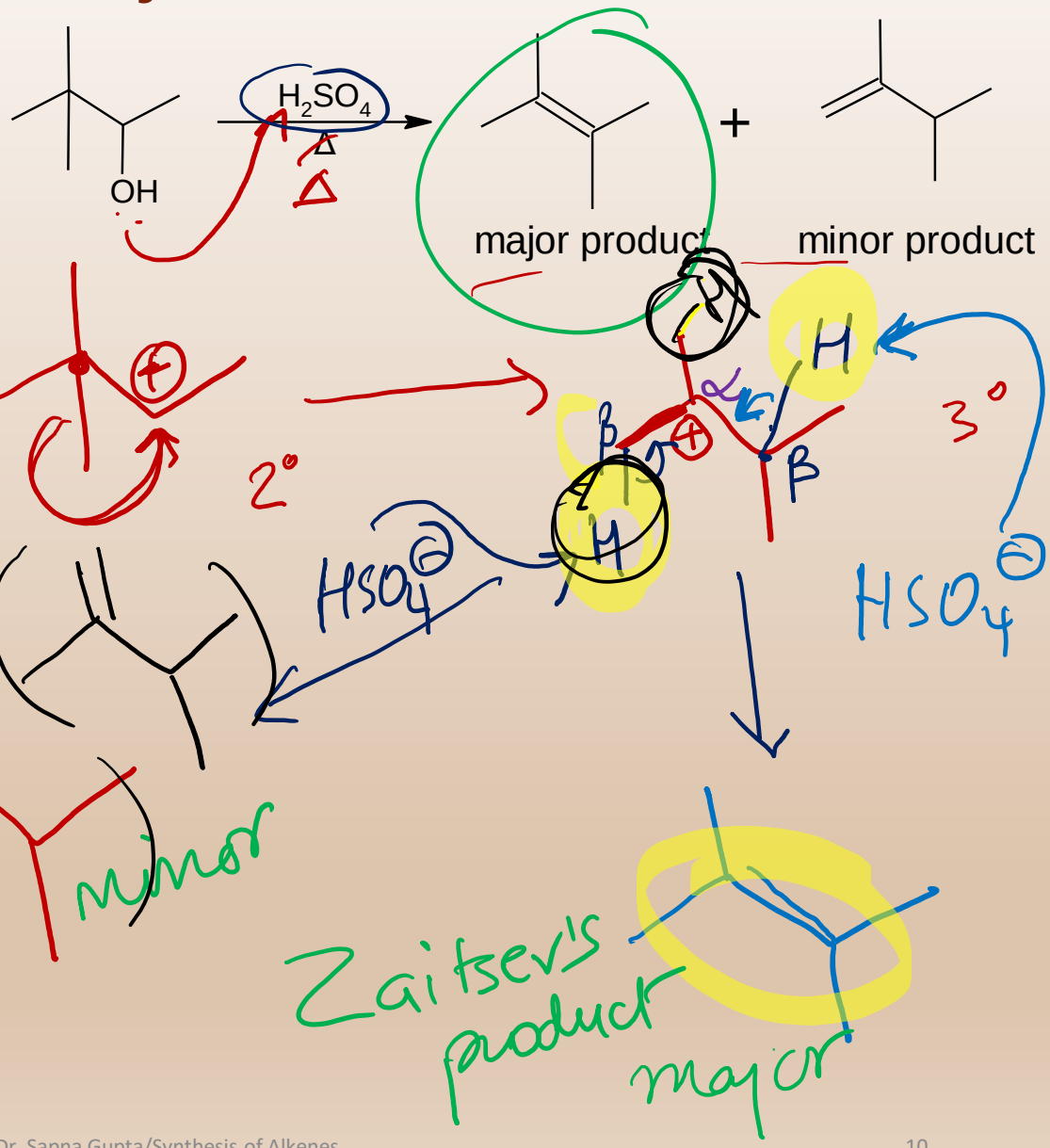
- Recall the stability of carbocations is:



- The second step of the E1 mechanism in which the carbocation forms is rate determining
- **Tertiary alcohols** react the **fastest** because they have the most stable tertiary carbocation-like transition state in the second step
- The mechanism for primary alcohols is E2 because primary carbocations are not stable

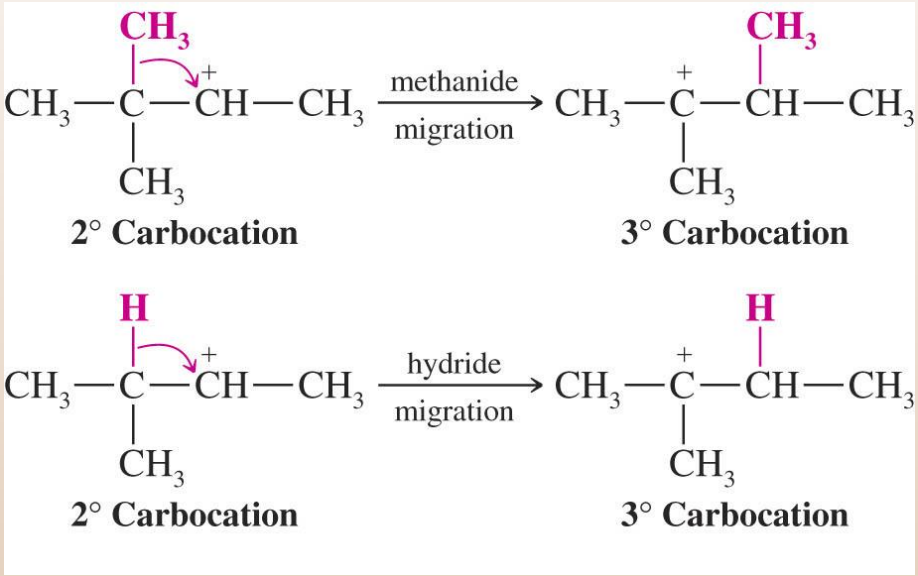
Rearrangement in Dehydration Reaction

- Rearrangements of carbocations occur if a more stable carbocation can be obtained

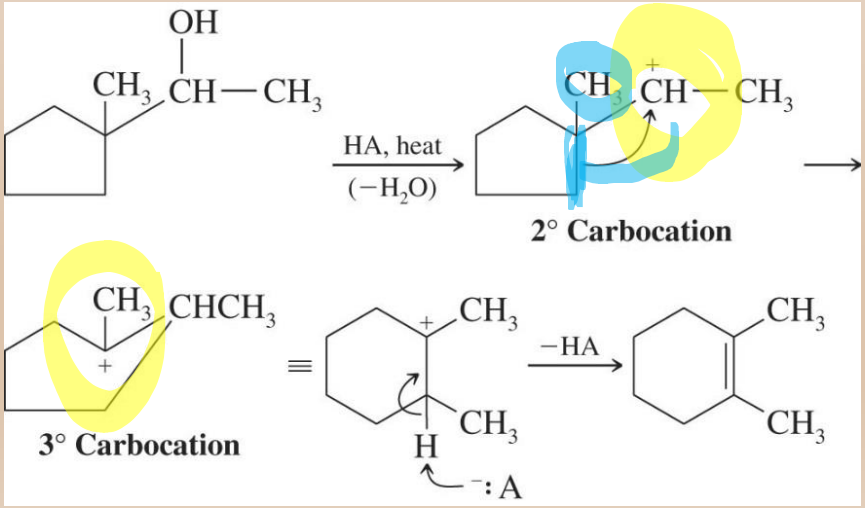


Some More Rearrangements

- Shifts can be hydride (hydrogen), methyl, phenyl
- Shifts occur only once

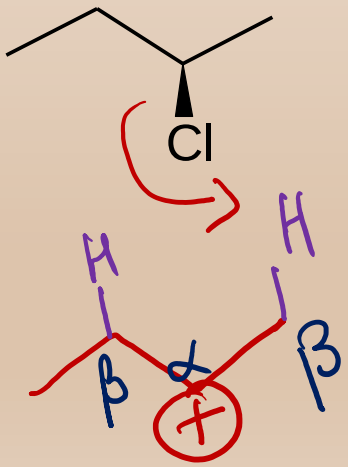


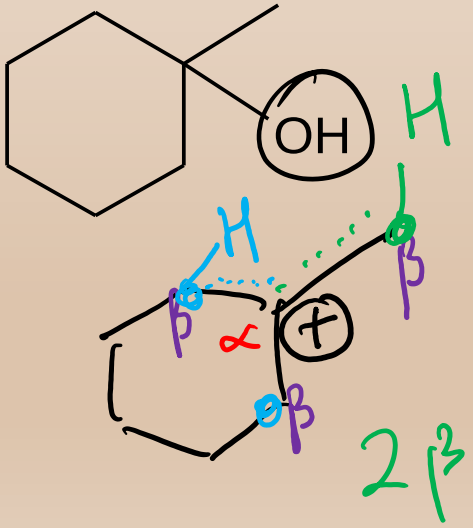
- Rearrangements can also cause change in the ring size

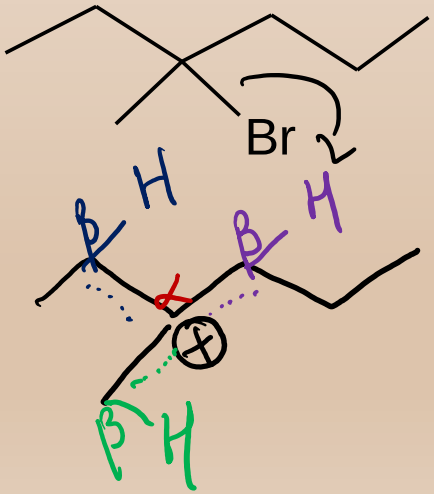


Identifying Hs to Eliminate

- All eliminations are α β or 1, 2, where α carbon or 1 carbon has the LG and β carbon or 2 carbon has the H.
- It is important to identify ALL the β H that can be eliminated in order to form ALL the products.
- Some of the products may be major, some minor, but still, one has to know all the β Hs.







Key Words/Concepts

- Elimination Reaction
- Base
- Leaving group
- 1^{st} order reaction (unimolecular)
- 2^{nd} order reaction (bimolecular)
- Transition state
- Rate determining step
- Carbocation
- Solvent considerations
- Zaitsev's product
- Hoffman product