SRM
UNIVERSITY
(Under section 3 of UGC Act 1956)

CHAPTER-6
DEHYDROHALOGENATION OF ALKYL HALIDES

BY,
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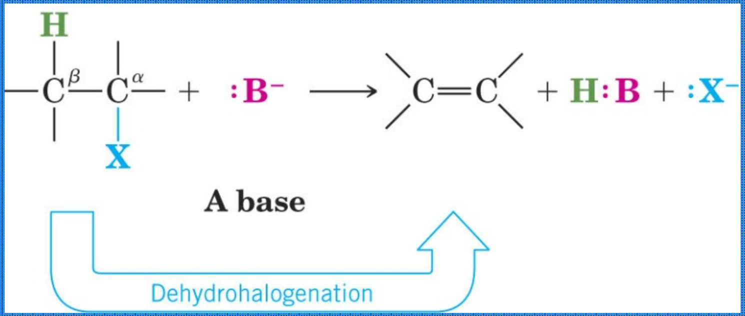
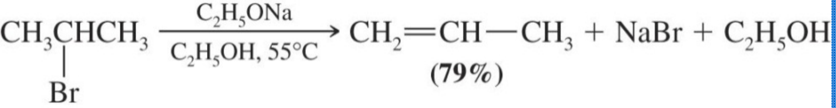
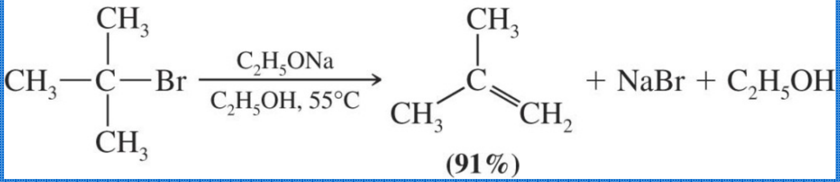
- Elimination Reactions of Alkyl Halides
  - Dehydrohalogenation
    - Used for the synthesis of alkenes
      - Elimination competes with substitution reaction
      - Strong bases such as alkoxides favor elimination



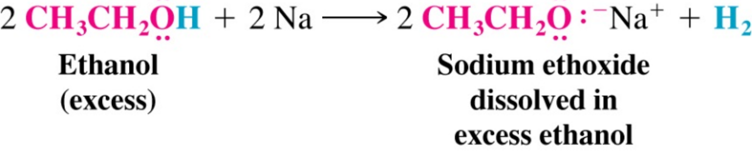


$$CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow[C_2H_5OH,\ 55°C]{C_2H_5ONa} CH_2{=}CH{-}CH_3 + NaBr + C_2H_5OH$$

(79%)



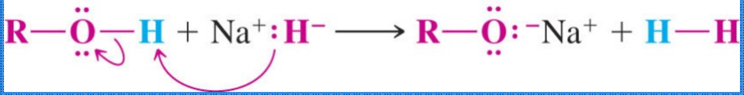
- The alkoxide bases are made from the corresponding alcohols



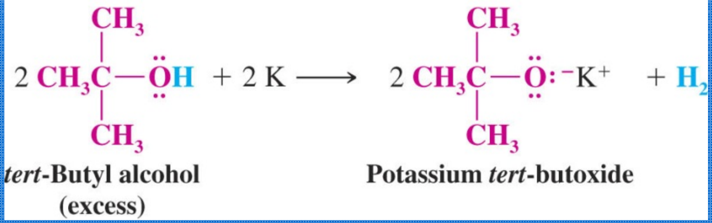
$$2\,CH_3CH_2\underset{\cdot\cdot}{\ddot{O}}H + 2\,Na \longrightarrow 2\,CH_3CH_2\underset{\cdot\cdot}{\ddot{O}}\!:^{-}Na^{+} + H_2$$

Ethanol (excess)

Sodium ethoxide dissolved in excess ethanol



$$R{-}\underset{\cdot\cdot}{\ddot{O}}{-}H + Na^{+}\!:\!H^{-} \longrightarrow R{-}\underset{\cdot\cdot}{\ddot{O}}\!:^{-}Na^{+} + H{-}H$$



$$2\,CH_3\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{\cdot\cdot}{\ddot{O}}H + 2\,K \longrightarrow 2\,CH_3\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{\cdot\cdot}{\ddot{O}}\!:^{-}K^{+} + H_2$$

***tert*-Butyl alcohol (excess)**

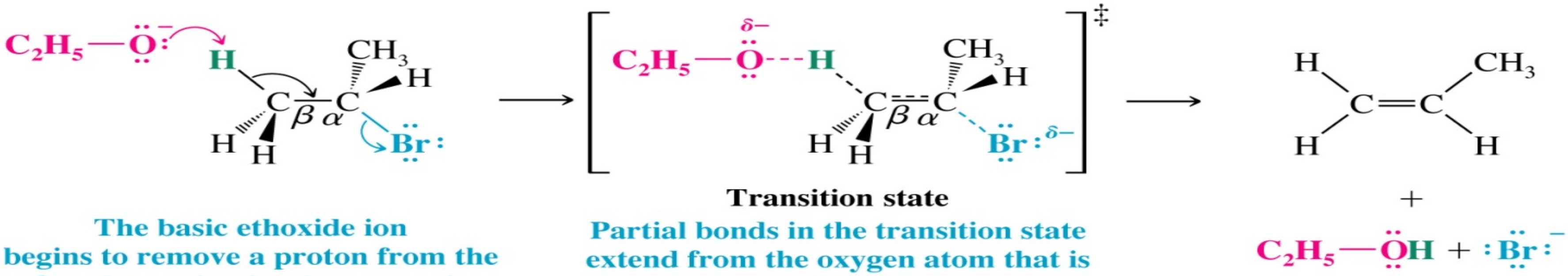
Potassium *tert*-butoxide

- The E2 Reaction
  - E2 reaction involves concerted removal of the proton, formation of the double bond, and departure of the leaving group
  - Both alkyl halide and base concentrations affect rate and
  - therefore the reaction is 2nd order

Reaction:

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

Mechanism:



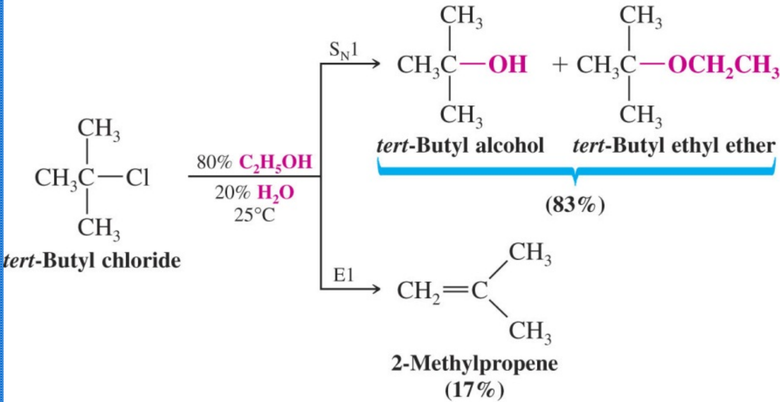
Transition state

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

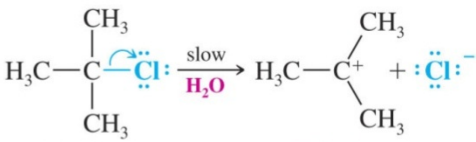
Partial bonds in the transition state extend from the oxygen atom that is removing the β hydrogen, through the carbon skeleton of the developing double bond, to the departing leaving group. The flow of electron density is from the base toward the leaving group as an electron pair fills the π bonding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

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.

- The E1 Reaction
    - The E1 reaction competes with the S_N1 reaction and likewise goes through a carbocation intermediate



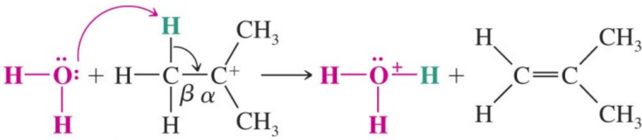
Step 1



Aided by the polar solvent, a chlorine departs with the electron pair that bonded it to the carbon.

This slow step produces the relatively stable 3° carbocation and a chloride ion. The ions are solvated (and stabilized) by surrounding water molecules.

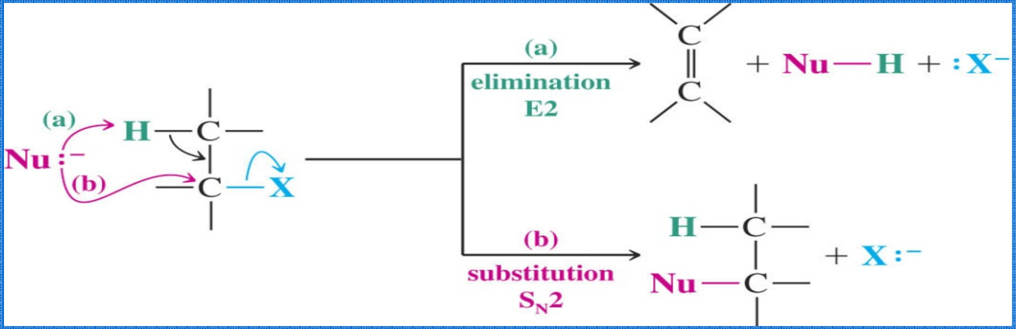
Step 2



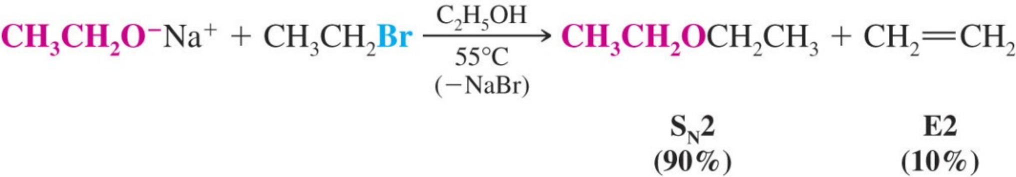
A molecule of water removes one of the hydrogens from the β carbon of the carbocation. These hydrogens are acidic due to the adjacent positive charge. At the same time an electron pair moves in to form a double bond between the α and β carbon atoms.

This step produces the alkene and a hydronium ion.

- Substitution versus Elimination
  - S_N2 versus E2

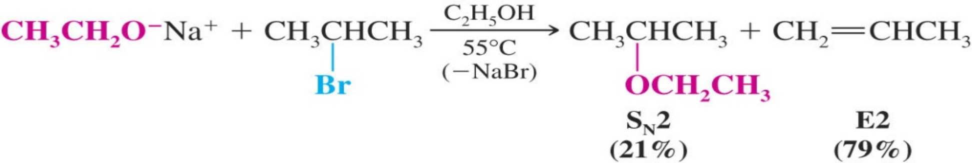


- Primary substrate
  - If the base is small, S_N2 competes strongly because approach at carbon is unhindered



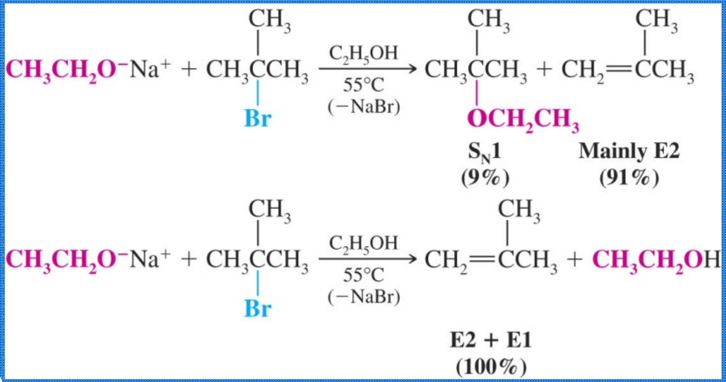
$$CH_3CH_2O^-Na^+ + CH_3CH_2Br \xrightarrow[\substack{55°C \\ (-NaBr)}]{C_2H_5OH} \underset{\substack{S_N2 \\ (90\%)}}{CH_3CH_2OCH_2CH_3} + \underset{\substack{E2 \\ (10\%)}}{CH_2{=}CH_2}$$

- Secondary substrate
  - Approach to carbon is sterically hindered and E2 elimination is favored

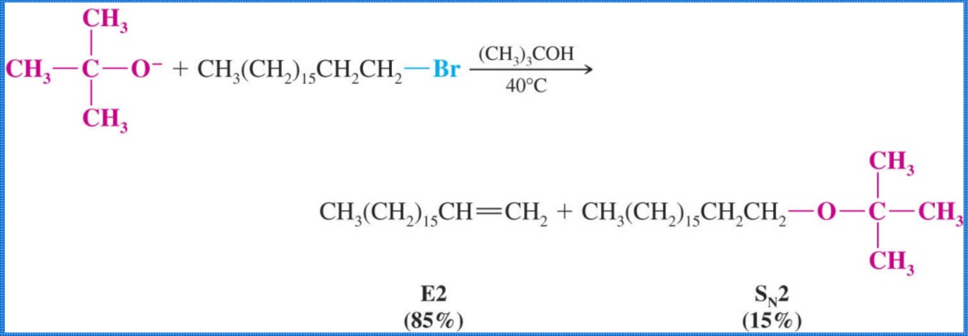


$$CH_3CH_2O^-Na^+ + \underset{\substack{| \\ Br}}{CH_3CHCH_3} \xrightarrow[\substack{55°C \\ (-NaBr)}]{C_2H_5OH} \underset{\substack{| \\ OCH_2CH_3 \\ S_N2 \\ (21\%)}}{CH_3CHCH_3} + \underset{\substack{E2 \\ (79\%)}}{CH_2{=}CHCH_3}$$

- Tertiary substrate
  - Approach to carbon is extremely hindered and elimination predominates especially at high temperatures

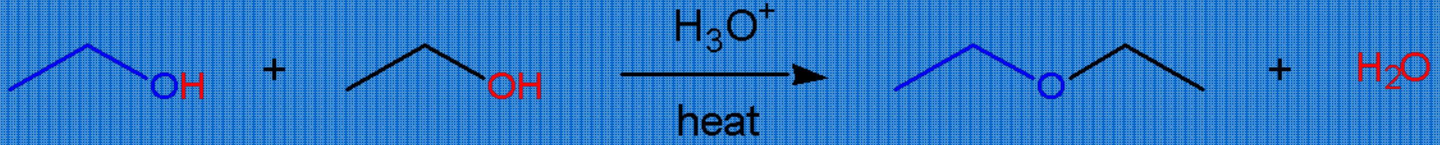


- Temperature
  - Increasing temperature favors elimination over substitution
- Size of the Base/Nucleophile
  - Potassium *tert*-butoxide is an extremely bulky base and is routinely used to favor E2 reaction

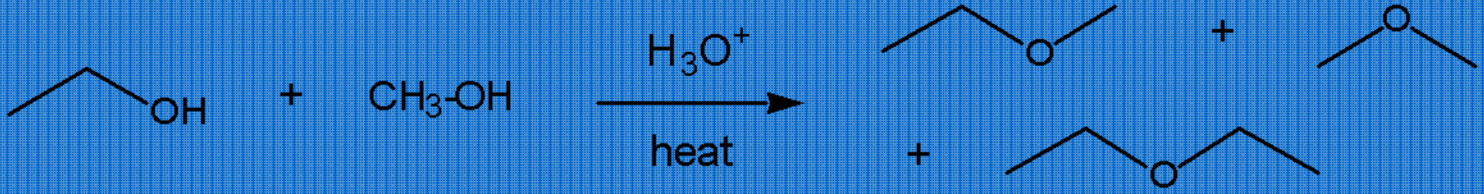


Dehydration of Alcohols to form Ethers

- Simple, symmetrical ethers can be formed from the intermolecular acid-catalyzed dehydration of 1° (or methyl) alcohols (a "substitution reaction")
- 2° and 3° alcohols can't be used because they eliminate (intramolecular dehydration) to form alkenes



- Unsymmetrical ethers can't be made this way because a mixture of products results:



THANK YOU