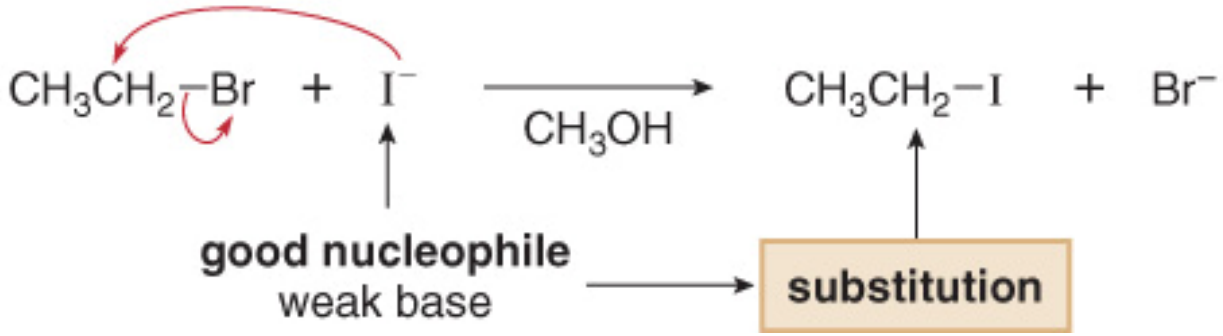
Alkyl Halides and Elimination Reactions

Predicting the Mechanism from the Reactants—S_N1, S_N2, E1 or E2.

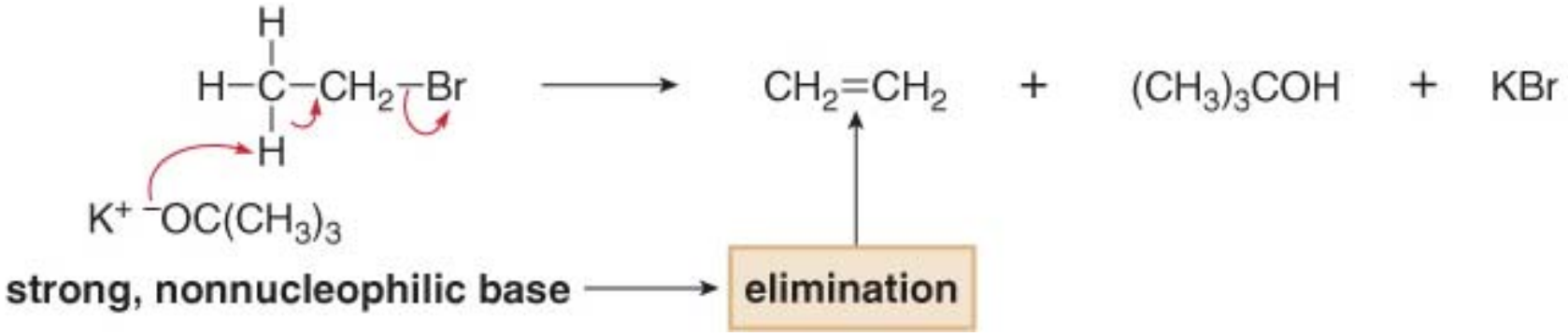
- **Good nucleophiles that are weak bases favor substitution over elimination—Certain anions generally give products of substitution because they are good nucleophiles but weak bases. These include I^-, Br^-, HS^-, ^-CN, and CH_3COO^-.**



Alkyl Halides and Elimination Reactions

Predicting the Mechanism from the Reactants—S_N1, S_N2, E1 or E2.

- **Bulky nonnucleophilic bases favor elimination over substitution—$KOC(CH_3)_3$, DBU, and DBN are too sterically hindered to attack tetravalent carbon, but are able to remove a small proton, favoring elimination over substitution.**

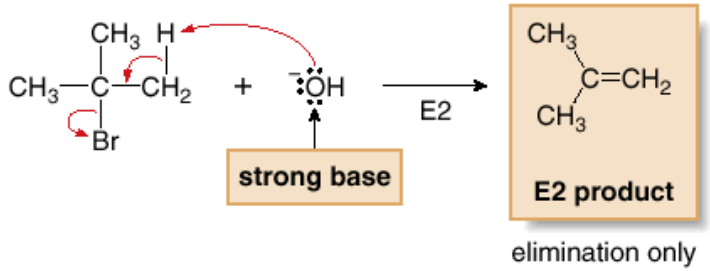


Predicting the Mechanism from the Reactants — S_N1, S_N2, E1 or E2

Figure 8.10 Determining whether an alkyl halide reacts by an S_N1, S_N2, E1, or E2 mechanism

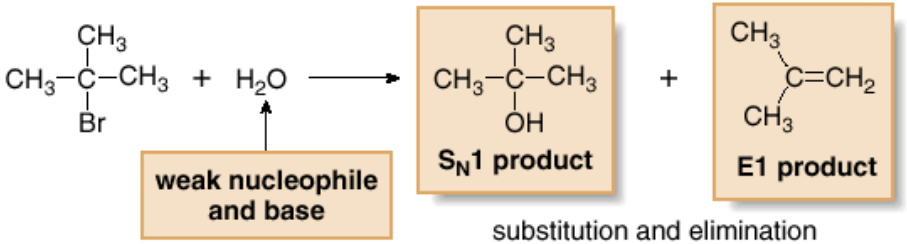
[1] 3° Alkyl halides (R_3CX react by all mechanisms except S_N2.)

- With strong bases
  - **Elimination occurs by an E2 mechanism.**
  - Rationale: A strong base or nucleophile favors an S_N2 or E2 mechanism, but 3° halides are too sterically hindered to undergo an S_N2 reaction, so only E2 elimination occurs.
  - Example:



elimination only

- With weak nucleophiles or bases
  - **A mixture of S_N1 and E1 products results.**
  - Rationale: A weak base or nucleophile favors S_N1 and E1 mechanisms, and both occur.
  - Example:



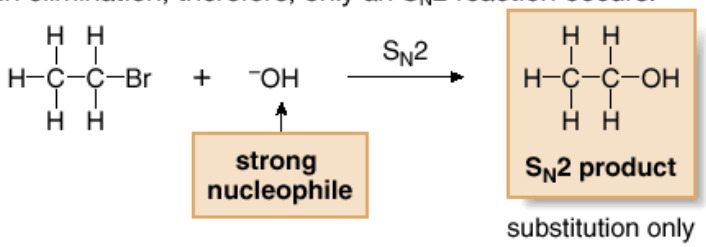
substitution and elimination

Predicting the Mechanism from the Reactants — S_N1, S_N2, E1 or E2

Figure 8.10 *continued*

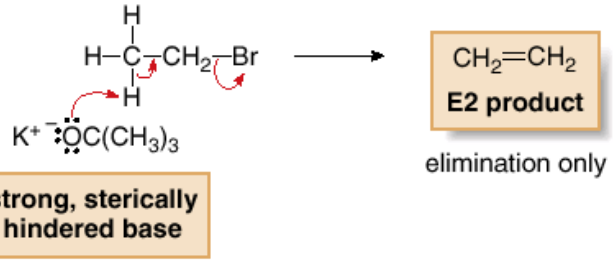
[2] 1° Alkyl halides (RCH_2X react by S_N2 and E2 mechanisms.)

- With strong nucleophiles
  - **Substitution occurs by an S_N2 mechanism.**
  - Rationale: A strong base or nucleophile favors S_N2 or E2, but 1° halides are the least reactive halide type in elimination; therefore, only an S_N2 reaction occurs.
  - Example:



substitution only

- With strong, sterically hindered bases
  - **Elimination occurs by an E2 mechanism.**
  - Rationale: A strong, sterically hindered base cannot act as a nucleophile, so elimination occurs and the mechanism is E2.
  - Example:



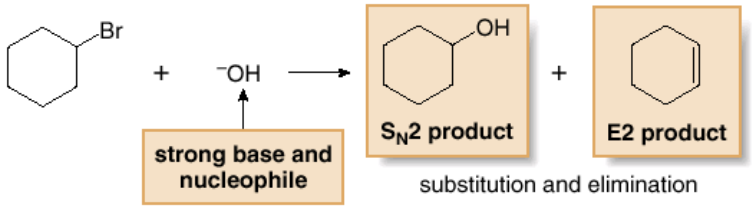
elimination only

Predicting the Mechanism from the Reactants — S_N1, S_N2, E1 or E2

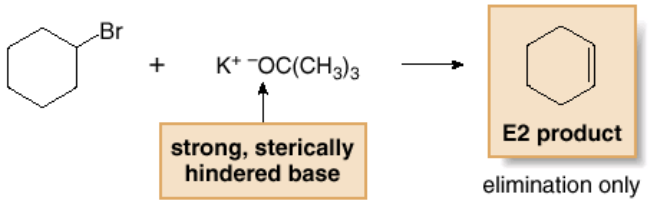
Figure 8.10 *continued*

[3] 2° Alkyl halides (R_2CHX react by all mechanisms.)

- With strong bases and nucleophiles
  - **A mixture of S_N2 and E2 products results.**
  - Rationale: A strong base that is also a strong nucleophile gives a mixture of S_N2 and E2 products.
  - Example:



- With strong, sterically hindered bases
  - **Elimination occurs by an E2 mechanism.**
  - Rationale: A strong, sterically hindered base cannot act as a nucleophile, so elimination occurs and the mechanism is E2.
  - Example:



- With weak nucleophiles or bases
  - **A mixture of S_N1 and E1 products results.**
  - Rationale: A weak base or nucleophile favors S_N1 and E1 mechanisms, and both occur.
  - Example: