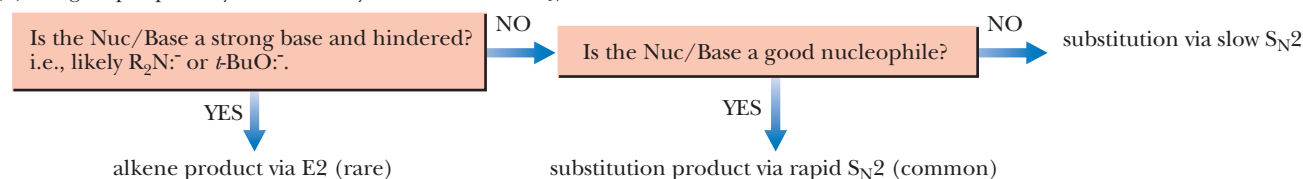


# Not For Sale

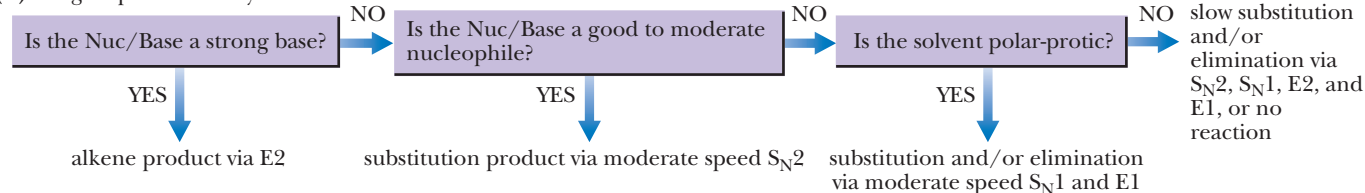
**Table 9.11** Summary of Substitution Versus Elimination Reactions of Haloalkanes

| Halide                              | Reaction                         | Comments   |
|-------------------------------------|----------------------------------|--|
| Methyl<br>$\text{CH}_3\text{X}$     | $\text{S}_{\text{N}}2$           | $\text{S}_{\text{N}}1$ reactions of methyl halides are never observed. The methyl cation is so unstable that it is not observed in common solvents.                                      |
| Primary<br>$\text{RCH}_2\text{X}$   | $\text{S}_{\text{N}}2$           | The main reaction with good nucleophiles/weak bases such as $\text{I}^-$ and $\text{CH}_3\text{COO}^-$ .   |
|                                     | E2                               | The main reaction with strong, bulky bases such as $(\text{CH}_3)_3\text{CO}^-$ .  |
|                                     | $\text{S}_{\text{N}}1/\text{E1}$ | Primary cations are rarely formed in solution, and, therefore, $\text{S}_{\text{N}}1$ and E1 reactions of primary halides are unlikely.  |
| Secondary<br>$\text{R}_2\text{CHX}$ | $\text{S}_{\text{N}}2$           | The main reaction with bases/nucleophiles where $\text{p}K_{\text{a}}$ of the conjugate acid is 11 or less, as for example $\text{I}^-$ and $\text{CH}_3\text{COO}^-$ .                  |
|                                     | E2                               | The main reaction with bases/nucleophiles where the $\text{p}K_{\text{a}}$ of the conjugate acid is 11 or greater, as for example $\text{OH}^-$ and $\text{CH}_3\text{CH}_2\text{O}^-$ . |
|                                     | $\text{S}_{\text{N}}1/\text{E1}$ | Common in reactions with weak nucleophiles in polar protic solvents, such as water, methanol, and ethanol.   |
| Tertiary<br>$\text{R}_3\text{CX}$   | E2                               | Main reaction with strong bases such as $\text{HO}^-$ and $\text{RO}^-$ .  |
|                                     | $\text{S}_{\text{N}}1/\text{E1}$ | Main reactions with poor nucleophiles/weak bases if the solvent is polar protic.   |
|                                     | $\text{S}_{\text{N}}2$           | $\text{S}_{\text{N}}2$ reactions of tertiary halides are never observed because of the extreme crowding around the $3^\circ$ carbon.   |

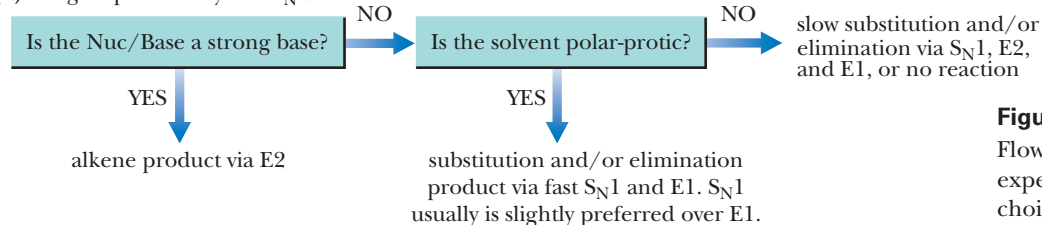
(a) R-group is primary and sterically unhindered: no  $\text{S}_{\text{N}}1$  or E1



(b) R-group is secondary



(c) R-group is tertiary: No  $\text{S}_{\text{N}}2$



**Figure 9.8**

Flow chart for determining the experimental conditions and choice of reagents that favor  $\text{S}_{\text{N}}2$ ,  $\text{S}_{\text{N}}1$ , E2, and E1 reactions.