

California State Polytechnic University, Pomona
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Ch. 7 Summary, Part 1 (Klein 4th Ed.): Alkyl Halides/Substitution Reactions

- I. Introduction to Alkyl Halides (7.1, 7.2)
 - a. Alkyl, vinyl, aryl halides
 - b. Substitution and Elimination reactions
- II. Substitution Reactions ($R-LG \rightarrow R-Nu$)
 - a. Electrophiles (E^+) (6.7)
 - i. Contain + or δ^+ sites (e.g., alkyl halides, carbocations)
 - b. Nucleophiles ($Nu:$) (6.7, 7.4)
 - i. Contain a source of electrons (e.g., lone pair or pi bond)
 - ii. More stable \rightarrow less reactive, weaker $Nu:$
 - iii. More electron-rich \rightarrow better $Nu:$
 - iv. Less electronegative \rightarrow better $Nu:$
 - v. Larger atom \rightarrow more polarizable, better $Nu:$
 - c. Leaving Groups (7.1, 7.10)
 - i. Stable species (weak bases) make good leaving groups (e.g., X^- , TsO^-)
 - ii. A good LG makes a favorable substitution reaction ($\Delta G < 0$)
 - iii. Make OH a good LG by protonation or tosylation (7.10)
- III. S_N2 mechanism (one step) (7.3) **SkillBuilders 7.1 & 7.2**
 - a. **Backside attack** with inversion of stereochemistry
 - b. Steric hindrance slows the S_N2 reaction
 - c. Requires good $Nu:$ (X^- , R_3N , CN^- , N_3^- , RS^- , RO^-)
- IV. S_N1 mechanism (7.8) **SkillBuilder 7.6**
 - a. Two key steps, via **carbocation**
 - b. More stable carbocation, faster S_N1 reaction
 - c. Racemization occurs, due to achiral intermediate
 - d. Reaction with water (H_2O) or alcohol (ROH) called solvolysis (3-step mechanism)
- V. S_N2 vs. S_N1
 - a. If an S_N2 can happen, it will happen! (S_N2 requires strong $Nu:$ and unhindered LG)
- VI. Competing Reactions
 - a. Carbocation rearrangements (6.11) **SkillBuilder 6.6**
 - b. Elimination reactions (loss of $H-X$ to form a pi bond) (**Chapter 7, Part 2**)
 - i. $E1$ – deprotonation of a carbocation (7.8, 7.10)
 - ii. $E2$ – one-step elimination of HX with a strong base (7.5, 7.7)
 - iii. Competition between all FOUR: Substitution (S_N1/S_N2) and Elimination ($E1/E2$)!
- VII. Solvent effects (7.12)

See Syllabus for suggested textbook problems

Summary of Chapter 7, Part 1 – Substitution Reactions

Alkyl Group (RX)	S_N1 (Carbocation!)	S_N2 (Backside Attack!)
3° (tertiary)	common	rare (N/R)
2° (secondary)	sometimes	sometimes
1° (primary)	rare (N/R)	common
CH ₃ (methyl)	never (N/R)	common
allyl or benzyl	common	common (if not 3°)