

Problem Set 5

1. Read Chapter 6 Section 1: You are responsible for recognizing alkyl halides and knowing the difference between alkyl halides, vinyl halides and aryl halides.

Work the following problem found in Section 1 of Chapter 6: **Problem 1.**

2. Read Chapter 6 Section 2: You should be familiar how to name alkyl halides using IUPAC nomenclature (*haloalkane*) as well as the common naming system (*alkyl halide*).

Work the following problems found in Section 2 of Chapter 6: **Problems 2 and 3.**

3. Read Chapter 6 Section 3: You should be familiar with the common uses of alkyl halides, particularly as solvents (why?) and as reagents/starting materials for organic reactions (why?).
4. Read Chapter 6 Sections 4 and 5: You should be familiar with the structure of alkyl halides, know why C-X (X = F, Cl, Br, I) bonds are polar, and know why the molecular structures of alkyl halides are polar as a result of polar C-X bonds if the molecule is not symmetrically substituted with halogens (e.g., CCl₄). You should be able to explain the physical properties of alkyl halides.

Work the following problems found in Section 4 and 5 of Chapter 6: **Problems 5-7.**

5. Read Chapter 6 Section 6: You are responsible for knowing how to prepare alkyl halides via free-radical halogenation using Cl₂ and Br₂ as a reagent. What are the steps involved in the reaction mechanism for free-radical halogenation? You should be familiar with the following: (1) the relative stabilities of 1°, 2° and 3° radical intermediates; (2) how those stabilities affect the reactivity of C-H bonds toward halogen radicals (•X); and (3) why free-radical halogenation is relatively nonselective—that is, why halogen radicals also react with C-H on 1° and 2° carbons despite the greater reactivity of C-H on 3° carbons. Read Chapter 4 Sections 2, 3, 6, 7, 9, 10, 13 and 16, which discuss free-radical halogenation in greater depth, including the how the mechanism of free-radical halogenation works, the relative strengths/reactivity of C-H, C-X and X-X bonds, the energetics (enthalpy) associated with bond breaking and formation, factors that affect the selectivity of halogen radicals (•X) in reacting with 1°, 2° and 3° C-H, and the how differences in the relative stabilities of carbon radical intermediates affect the reactivity of 1°, 2° and 3° C-H. Study Key Mechanism 4-1 for free-radical halogenation. What are the two steps involved in propagation leading to halogenation?

You are responsible for knowing how to prepare alkyl bromides via allylic bromination—that is bromination of C-H bonds on carbon atoms adjacent to C=C bonds (i.e., H-C-C=C). What is an allylic carbon? Why is the reactivity of C-H on allylic carbon atoms different from that of typical saturated carbon atoms? What role does the adjacent C=C bond play in stabilizing the carbon radical intermediate? What is resonance stabilization and how does resonance stabilization affect the C-H bond strength and reactivity at allylic positions? What is the reagent NBS (N-bromosuccinimide) and why is NBS in CCl₄ as solvent as a source of Br₂ for allylic bromination? What role does the CCl₄ solvent play with respect to the solubility of NBS? Why is it important to keep the concentration of Br₂ produced low in the reaction?

Work the following problems found in Section 6 of Chapter 6: **Problems 8-10.**

Work the following problems found in Sections 3, 6, 7, 13 and 16 of Chapter 4: **Problems 1, 2, 4, 9, 10, 14, 15, 18-21 and 30.**

Work the following problems found at the back of Chapter 6: **Problems 31, 32, 41b, 46a, 47, 50, 51, 57-59.**

Work the following problems found at the back of Chapter 4: **Problems 35-37, 40, 42-49.**