

Chemistry 210  
“Organic Chemistry I”  
Summer Semester 1999  
Dr. Rainer Glaser

Examination #2

“Alkyl Halides: Their Synthesis by Halogenation of Alkanes  
and Their Nucleophilic Substitution Reactions.”

Friday, July 9, 1999, 9:00 - 9:50

Name:

|                                                          |     |  |
|----------------------------------------------------------|-----|--|
| Question 1. Radical Chain Halogenations I.               | 14  |  |
| Question 2. Radical Chain Halogenations II. (MC #4)      | 16  |  |
| Question 3. Stereochemistry I. (incl. News #5)           | 14  |  |
| Question 4. Stereochemistry II. (MC #5)                  | 16  |  |
| Question 5. Nucleophilic Substitution I. (incl. News #6) | 12  |  |
| Question 6. Nucleophilic Substitution II. (VC #6)        | 12  |  |
| Question 7. Nucleophilic Substitution III. (MC #6)       | 16  |  |
| Total                                                    | 100 |  |
| Multiple Choice Percentage Q2, Q4 and Q7.                |     |  |

**Question 1. Radical Chain Halogenations I. (14 points)**

(a) Consider the **monochlorination** of n-butane,  $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ . Write down the structures of both possible products. Circle the structure that is **statistically** more likely to be produced. (4 points)

[illegible]

**(b)** Consider the **monobromination** of n-butane,  $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ . Write down the structures of both possible products. Circle the structure that is produced as the **major product**. (4 points)

[illegible]

**(c)** The first propagation step in the radical chain halogenation of alkanes involves the abstraction of an H-atom by a halogen radical. The differences in the selectivities in the radical chain chlorination and bromination of alkanes has to do with the differences in the first propagation step. Schematically, draw the transition state structures for the abstraction of H from methane by chlorine and by bromine. For each transition state structure indicate whether the transition state is “early” or “late.” Your drawings should reflect whether the TS is early or late by appropriate XC and CH distances. (6 points)

|                                               |                                              |
|-----------------------------------------------|----------------------------------------------|
| TS(Chlorine radical abstracts H from methane) | TS(Bromine radical abstracts H from methane) |
|-----------------------------------------------|----------------------------------------------|

**Question 2.** Radical Chain Halogenations II and Thermodynamics and Kinetics. (16 points)

PE1-Q1 What products are obtained in disproportionation of the isopropyl radical,  $\text{CH}_3\text{-CH}\cdot\text{-CH}_3$ ?

- a. Propene and propane
- b. Propene and hydrogen atom
- c. Two propene molecules and hydrogen molecule
- d. Ethyl radical and butyl radical
- e. Ethene and butane

PE1-Q2 Which equation correctly expresses the relation between the equilibrium constant  $K$  and the free energy of reaction?

- a.  $G = -RT\ln(\Delta K)$
- b.  $\Delta G = -RT\ln(K)$
- c.  $\Delta G = -Rt\log(K)$
- d.  $\Delta G = +RT\ln(\Delta K)$
- e.  $G = +RT\log(K)$

PE1-Q5 Which one of the following reaction steps describes the rate limiting propagation step of the bromination of methane?

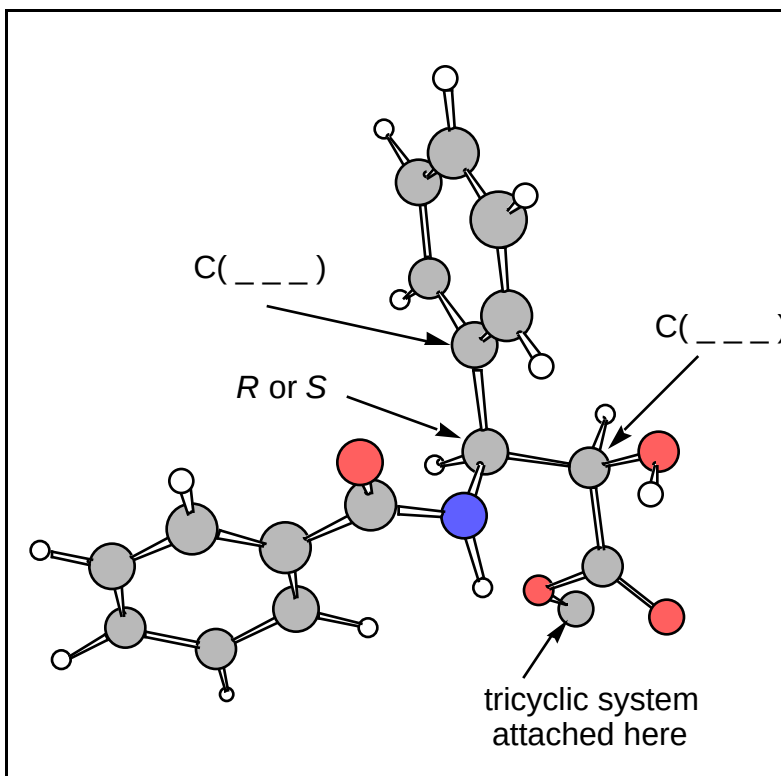
- a.  $\text{Br-Br} \xrightarrow{\text{light}} 2 \text{Br}\cdot$
- b.  $\text{Br}\cdot + \text{CH}_4 \rightarrow \text{H-Br} + \cdot\text{CH}_3$
- c.  $\cdot\text{CH}_3 + \text{Br-Br} \rightarrow \text{Br-CH}_3 + \text{Br}\cdot$
- d.  $\text{Br}\cdot + \cdot\text{CH}_3 \rightarrow \text{BrCH}_3$
- e.  $\text{Br}\cdot + \cdot\text{H} \rightarrow \text{HBr}$

PE1-Q12 In what ratio are 1-bromobutane and 2-bromobutane produced in the bromination of butane?

- a. 1-bromobutane : 2-bromobutane = 1 : 65
- b. 1-bromobutane : 2-bromobutane = 65 : 1
- c. 1-bromobutane : 2-bromobutane = 1 : 97
- d. 1-bromobutane : 2-bromobutane = 97 : 1
- e. 1-bromobutane : 2-bromobutane = 1 : 1

**Question 3. Stereochemistry I. (14 points)**

(a) The article “BRISTOL-MYERS TAXOL WINS FDA NOD FOR KAPOSI’S SARCOMA” (*Bloomberg News*, Aug. 7, **1997**) talked about the importance of the right chirality for the desired drug action to occur. On the right, a molecular model of a **fragment of taxol** is shown. Name the indicated chiral C-atom with the *R/S* nomenclature; **circle R or S**, and **fill in the blanks** in the lists “C( \_ \_ \_ )” you use in applying the **sequence rules**. Clearly indicate the **priorities** of the four substituents (give the number 1-4). Note: The hetero-atom directly attached to the C to be named is an N-atom; all other hetero-atoms are O-atoms.



The enantiomers of taxol have different effects because they bind to different receptors. Receptors are themselves chiral. **Chiral recognition** occurs because the aggregates formed between the enantiomers and a given receptor are \_\_\_\_\_ (enantiomers, diastereoisomers) and they have \_\_\_\_\_ (the same, different) energies. (5 points)

(b) For the cyclobutane shown, mark every asymmetric carbon by a star (\*). For each of these asymmetric carbons, indicate the absolute configuration using the *R/S* nomenclature system. Then draw the enantiomer and one diastereoisomer and, for both, also indicate the absolute configuration of all asymmetric carbons with the *R/S* nomenclature system. (9 points)

| The cyclobutane | Draw the <b>enantiomer</b> | Draw one <b>diastereoisomer</b> |
|-----------------|----------------------------|---------------------------------|
|                 |                            |                                 |

**Question 4. Stereochemistry II. (16 points)**

E-Q7 Complete the sentence: A chiral carbon has *R* configuration if ...

- a. the substituents with priorities 1, 2, and 3 are arranged counterclockwise when viewed in the direction  $C^* \rightarrow 4$
- b. the substituents with priorities 1, 2 and 3 are arranged clockwise when viewed in the direction  $C^* \rightarrow 4$
- c. the substituents with priorities 2, 3 and 4 are arranged clockwise when viewed in the direction  $C^* \rightarrow 1$
- d. the substituents with priorities 2, 3 and 4 are arranged counterclockwise when viewed in the direction  $C^* \rightarrow 1$
- e. the substituents with priorities 1, 2 and 4 are arranged counterclockwise when viewed in the direction  $C^* \rightarrow 3$

E-Q8 Select the substituent with the highest priority.

- a.  $-\text{CH}_2\text{-OH}$
- b.  $-\text{CH=O}$
- c.  $-\text{CH}_2\text{-CH}_2\text{-OH}$
- d.  $-\text{CH}_2\text{-CH=O}$
- e.  $-\text{CH}_2\text{-OCH}_3$

E-Q13 Which equation is used to compute the specific rotation?

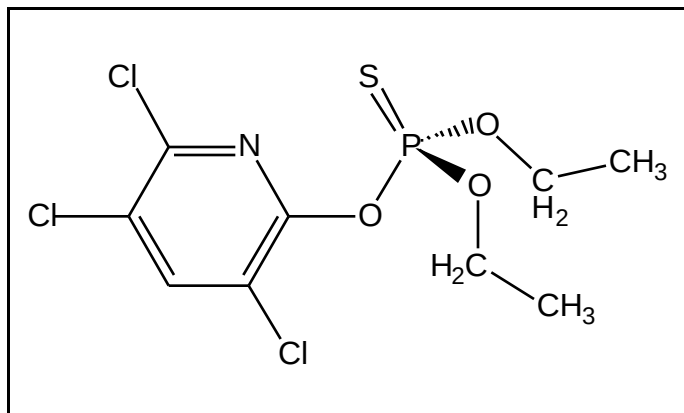
- a.  $\alpha / (\text{cell length} \times \text{concentration})$
- b.  $\alpha \times \text{cell length} \times \text{concentration}$
- c.  $(\alpha \times \text{cell length}) / \text{concentration}$
- d.  $\alpha \times \text{cell length}$
- e.  $\alpha \times \text{concentration}$

E-Q14 What is the relation between the configuration and the optical rotation?

- a. *R* compounds always are dextrorotatory
- b. *R* compounds always are levorotatory
- c. *R* compounds usually are dextrorotatory with few exceptions
- d. *R* compounds usually are levorotatory with few exceptions
- e. There is no relation.

**Question 5. Nucleophilic Substitution I. (12 points)**

The article “BAN IS SOUGHT ON 5 PESTICIDES TO PROTECT KIDS” (*The Arizona Republic*, Jan. 29, 1998) talked about environmental activism aimed at banning a group of pesticides. One of these is **chlorpyrifos** and its structure is shown. This compound is suspected to be toxic because of its high “ethylating power.” **Chlorpyrifos** contains two ethyl groups. If one of these ethyl groups is

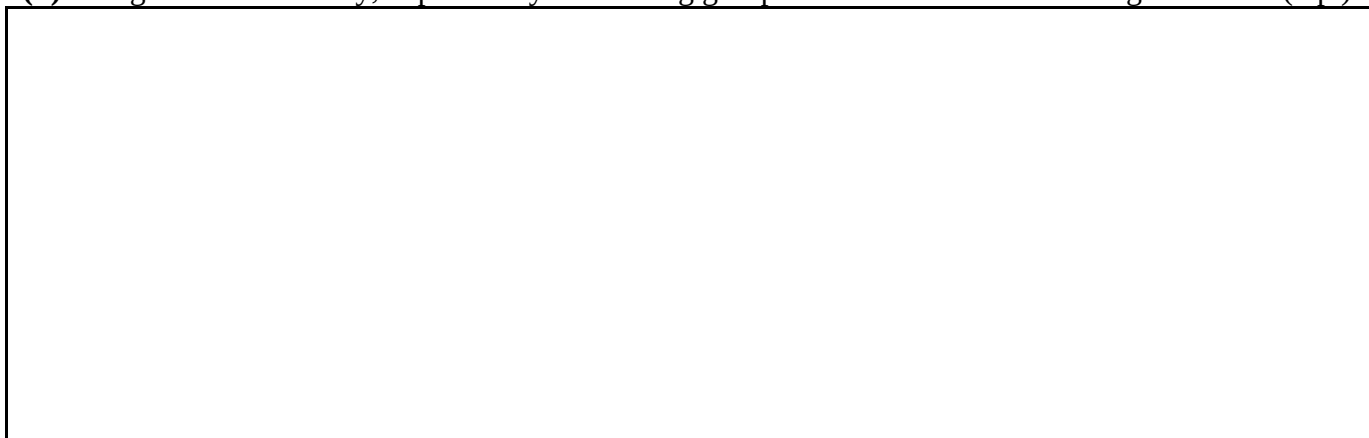


attacked by a nucleophile, then an \_\_\_\_\_ ( $S_N1$ ,  $S_N2$ ) reaction can occur. This  $S_N$  reaction is facilitated by the fact that the nucleofug is a really good leaving group. (2 point)

(a) Consider the reaction of the **methyl sulfide** nucleophile,  $H_3C-S^-$ , with **chlorpyrifos**. Draw the structure of the product of this reaction and draw the structure of the leaving group. (6 p.)

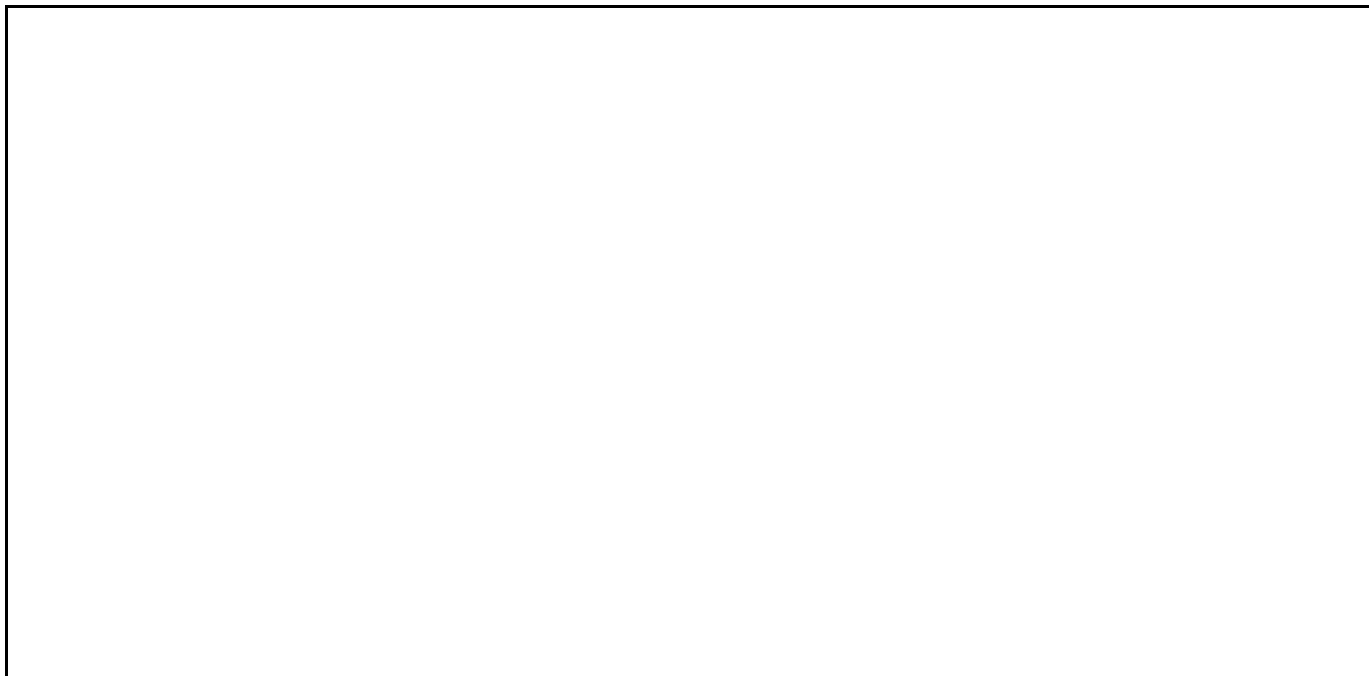


(b) Using resonance theory, explain why the leaving group in the above reaction is a “good” one. (4 p.)



**Question 6.** Nucleophilic Substitution II. (12 points)

(a) *Tertiary* butyl chloride can be converted into *tertiary* butanol by way of hydrolysis (cf. visualization center #6). Of course, this nucleophilic substitution reaction involves an \_\_\_\_\_ ( $S_N1$ ,  $S_N2$ ) reaction since the C-atom that carries the leaving group is \_\_\_\_\_ ( $1^\circ$ ,  $2^\circ$ ,  $3^\circ$ ) and since the nucleophile is rather \_\_\_\_\_ (weak, strong). Provide a mechanism for this reaction. Draw structures of the substrate, show all intermediates, and show the product. **In all structures, always show all atoms.** (8 points)



(b) Draw a potential energy diagram for the above reaction. Indicate which minima correspond to which structures (intermediate, product). Indicate the activation barrier for the slowest step (draw arrow). (4 points)



**Question 7. Nucleophilic Substitution III. (16 points)**

- E-Q1 Which statement best characterizes the polarity of a C-Cl bond?
- Covalent and essentially non polar
  - Covalent and polar with chlorine carrying a partial positive charge
  - Covalent and polar with chlorine carrying a partial negative charge
  - Ionic and polar with chlorine carrying essentially a full positive charge
  - Ionic and polar with chlorine carrying essentially a full negative charge
- E-Q3 Which rate law describes bimolecular nucleophilic substitution reactions?
- Rate =  $k$  [alkyl halide] [nucleophile]
  - Rate =  $k$  [nucleophile]<sup>2</sup>
  - Rate =  $k$  [alkyl halide]<sup>2</sup>
  - Rate =  $k$  [alkyl halide] [nucleophile]<sup>2</sup>
  - Rate =  $k$  [alkyl halide]<sup>2</sup> [nucleophile]
- E-Q10 Which type of substrate shows the highest reactivity in SN2 reactions?
- Methyl halide
  - Primary alkyl halide
  - Secondary alkyl halide
  - Tertiary alkyl halide
  - Quaternary alkyl halide
- E-Q18 Suppose the double bonded methylene group of 1-bromo-2-propene is labeled with <sup>13</sup>C, H<sub>2</sub><sup>13</sup>C=CH-CH<sub>2</sub>-Br. What product will be formed by methanolysis of this substrate?
- H<sub>2</sub><sup>13</sup>C=CH-CH<sub>2</sub>-OCH<sub>3</sub>
  - H<sub>2</sub>C=CH-<sup>13</sup>CH<sub>2</sub>-OCH<sub>3</sub>
  - H<sub>2</sub><sup>13</sup>C=CH-CH<sub>2</sub>-OCH<sub>3</sub> and H<sub>2</sub>C=CH-<sup>13</sup>CH<sub>2</sub>-OCH<sub>3</sub>
  - H<sub>2</sub>C=<sup>13</sup>CH-CH<sub>2</sub>-OCH<sub>3</sub>