

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

Examination #2

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

Friday, March 12, 1999, 9:00 - 9:50

Name:

Answer Key

Question 1. Radical Chain Halogenations I.	12	
Question 2. Radical Chain Halogenations II.	16	
Question 3. Stereochemistry I. (incl. News #5)	14	
Question 4. Stereochemistry II.	16	
Question 5. Nucl. Subst. & Elim. I. (incl. News #6)	12	
Question 6. Nucl. Subst. & Elim. II.	14	
Question 7. Nucl. Subst. & Elim. III.	16	
Total	100	
Multiple Choice Percentage Q2, Q4 & Q7.		

Question 1. Radical Chain Halogenations I. (12 points)

(a) Consider the **monochlorination** of propane. Write down the structures of both possible products. Circle the structure that is **statistically** more likely to be produced. (3 points)

Draw structures of 1-chloropropane and 2-chloropropane.

Circle the structure of 1-chloropropane.

6 methyl H-atoms and only 2 methylene H-atoms.

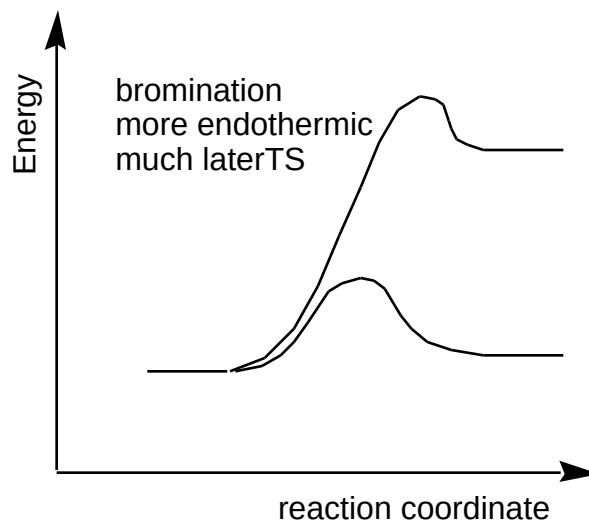
(b) Consider the **monobromination** of propane. Write down the structures of both possible products. Circle the structure that is produced as the **major product**. (3 points)

Draw structures of 1-bromopropane and 2-bromopropane.

Circle the structure of 2-bromopropane.

Highly selective for the more substituted C-atom!

(c) The radical chain halogenation of alkanes involves two propagation steps. The first propagation step involves the abstraction of a hydrogen-atom from the alkane by a halogen-radical. In the second propagation step, an alkyl radical reacts with a halogen-molecule to give a product molecule and a new 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. Let's look at the first propagation step of the chlorination and the bromination of **methane**.



Draw the energy diagram for these processes. Make sure that your drawing (a) shows whether the reaction step is endothermic or exothermic, (b) shows which curves apply to chlorination and bromination, respectively, and (c) whether the transition state is “early” or “late”. You do not need to give the actual values for the activation barriers and reaction energies; but you are expected to produce a diagram that is correct qualitatively. (6 points)

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

E-Q3 Which one of the following equations correctly describes the homolytic bond cleavage of chlorine?

- a. $\text{Cl-Cl} \xrightarrow{-(200^\circ\text{C or infrared light})} 2 \text{Cl}$
- b. $\text{Cl-Cl} \xrightarrow{-(200^\circ\text{C})} \text{Cl}^+ + \text{Cl}^-$
- c. $\text{Cl-Cl} \xrightarrow{-(400^\circ\text{C or UV/Vis light})} 2 \text{Cl}^+$
- d. $\text{Cl-Cl} \xrightarrow{-(400^\circ\text{C or UV/Vis light})} \text{Cl}^+ + \text{Cl}^-$
- e. **$\text{Cl-Cl} \xrightarrow{-(400^\circ\text{C or UV/Vis light})} 2 \text{Cl}$**

E-Q8 What value of ΔG° is needed to obtain a conversion to product that is greater than 99%?

- a. +30 kcal/mol
- b. +3 kcal/mol
- c. 0 kcal/mol
- d. **-3 kcal/mol**
- e. -30 kcal/mol

E-Q12 Which molecule has the **lowest** C-H bond dissociation energy?

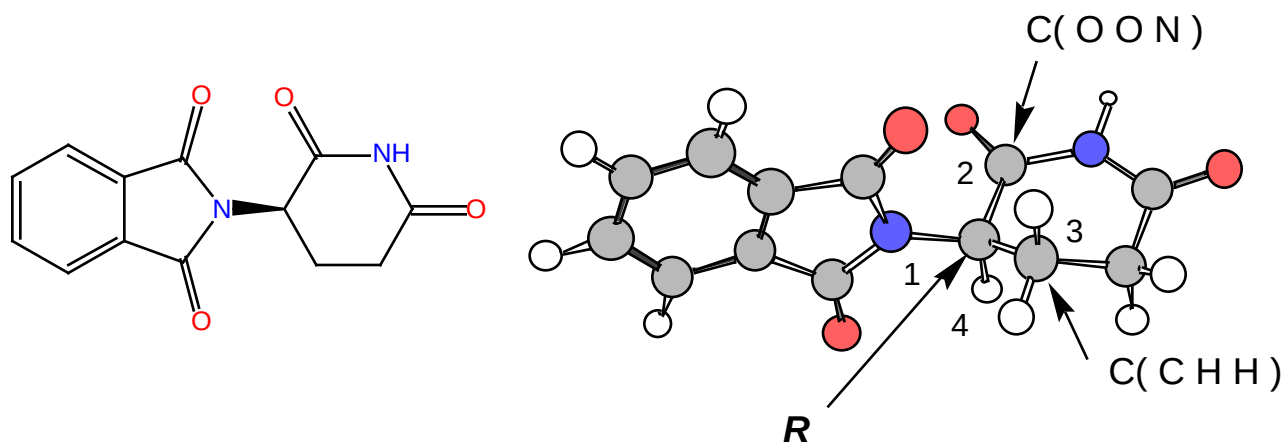
- a. Me-H (methyl)
- b. Et-H (primary)
- c. *Iso*-Pro-H (secondary)
- d. ***Tert.*-Bu-H (tertiary)**
- e. Ph-H (aromatic)

E-Q16 Which equation shows the **Arrhenius** equation?

- a. $k = A \exp(E_a/RT)$
- b. **$k = A \exp(-E_a/RT)$**
- c. $k = A \exp(R/E_a)$
- d. $k = A \exp(-R/E_a)$
- e. This option is not used.

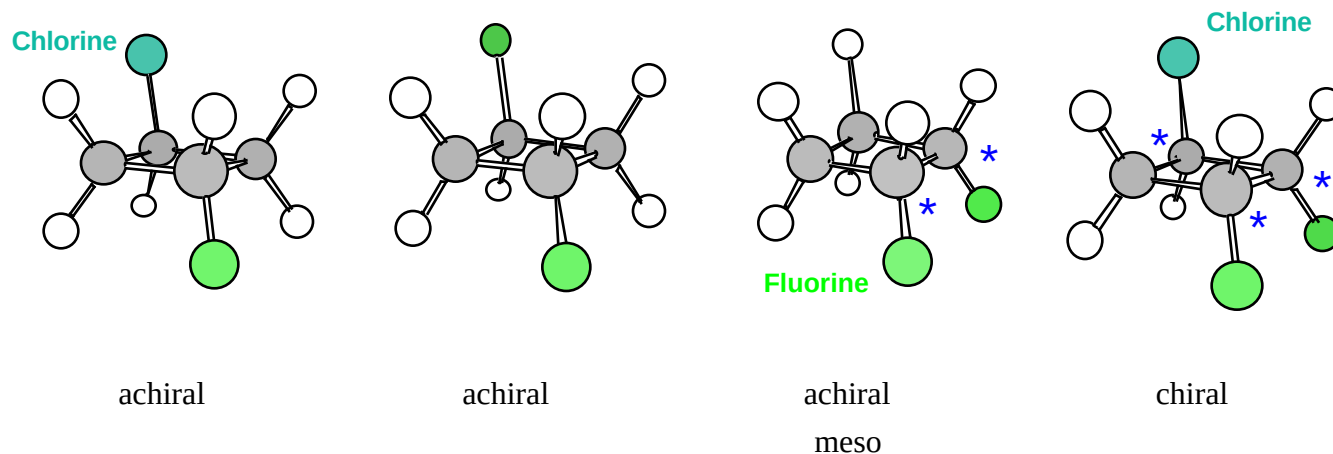
Question 3. Stereochemistry I. (14 points)

(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. The enantiomers of **thalidomide** were discussed in this context and one of these enantiomers is shown as a molecular model. Name this enantiomer according to 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.



The different enantiomers of thalidomide have such drastically 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 diastereoisomers (enantiomers, diastereoisomers) and they have different (the same, different) energies. (6 points)

(b) For each of the four structures, mark every chiral carbon with a star (if any). Indicate just below the molecule whether the molecule is chiral or achiral. If the molecule is a meso form, write the word “meso” just below that structure. (8 points)



Question 4. Stereochemistry II. (16 points)

PE1-Q2 Which of the objects **do** come as enantiomers?

- a. snow boards
- b. rowing boats
- c. planes
- d. trains
- e. automobiles**

Q3 Which is the correct ranking of the substituents.

- a. $-\text{CCl}_3 > -\text{CF}_3 > -\text{CHBr}_2 > -\text{CH}_2\text{I}$
- b. $-\text{CCl}_3 > -\text{CF}_3 > -\text{CH}_2\text{I} > -\text{CHBr}_2$
- c. $-\text{CCl}_3 > -\text{CH}_2\text{I} > -\text{CHBr}_2 > -\text{CF}_3$
- d. $-\text{CH}_2\text{I} > -\text{CHBr}_2 > -\text{CCl}_3 > -\text{CF}_3$**
- e. $-\text{CH}_2\text{I} > -\text{CCl}_3 > -\text{CF}_3 > -\text{CHBr}_2$

PE-Q8 What is the optical purity of a mixture that contains one quarter (*S*) enantiomer and three quarters (*R*) enantiomer?

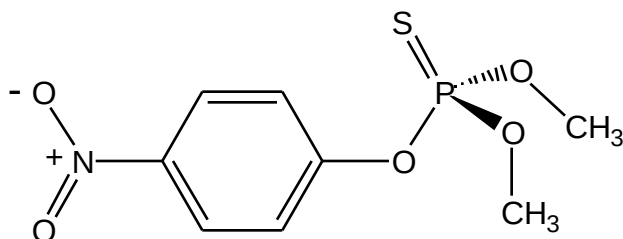
- a. 25 %
- b. 50 %**
- c. 75 %
- d. 90 %
- e. 95 %

PE1-Q11 With three chiral centers present, which pair of these stereoisomers is a pair of diastereoisomers?

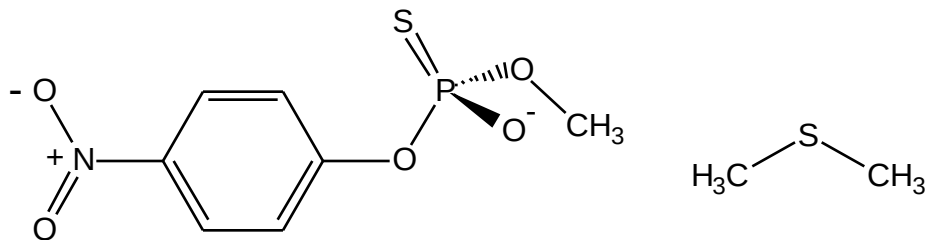
- a. (*R,R,R*) and (*S,S,S*)
- b. (*S,R,R*) and (*R,S,S*)
- c. (*R,R,S*) and (*S,S,R*)
- d. (*R,S,R*) and (*S,R,S*)
- e. (*S,S,R*) and (*R,S,R*)**

Question 5. Nucleophilic Substitution and Elimination I. (12 points)

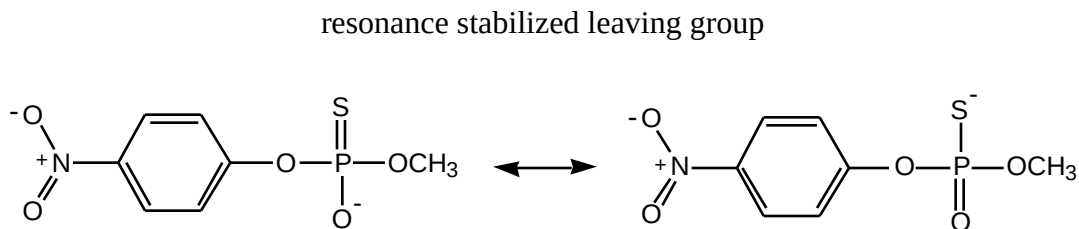
The article “BAN IS SOUGHT ON 5 PESTICIDES TO PROTECT KIDS” (*The Arizona Republic*, Jan. 29, **1998**) talked about environmental activism aimed at banning a group of pesticides. One of these is **methyl parathion** and its structure is shown. This compound is suspected to be toxic because of its high methylating power. Methyl parathion contains two methyl groups. If one of these methyl groups is attacked by a nucleophile, then an S_N2 (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. (1 point)



(a) Consider the reaction of the **methyl sulfide** nucleophile, H_3C-S^- , with methyl parathion. Draw the structure of the product of this reaction and draw the structure of the leaving group as well. (5 p.)

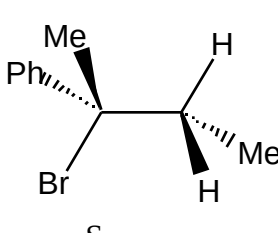
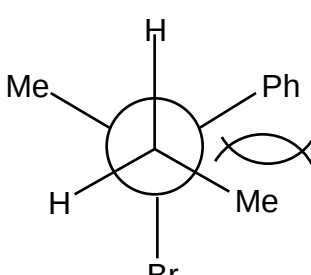
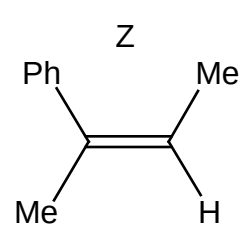
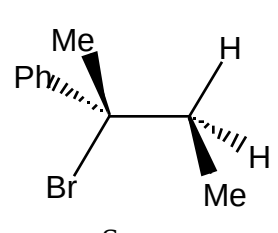
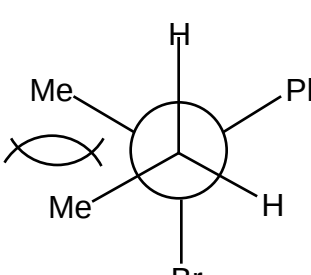
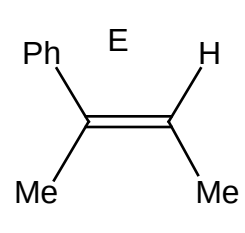


(b) Using resonance theory, explain why the leaving group in the above reaction is a “good” one. (6 p.)



Question 6. Nucleophilic Substitution and Elimination II. (14 points)

To begin with, the HBr elimination from 2-bromo-2-phenylbutane will give a 2-phenyl-2-butene and not 2-phenyl-1-butene because eliminations always give the more (more, less) substituted alkene; this is expressed in the Saytzeff rule. With the regiochemistry therefore clear, now let's look at the stereochemistry. Two *staggered* conformations are shown of the **same** molecule. Each of the conformations is suitable to undergo an antiperiplanar E2 elimination. Label all chiral centers according to the *R/S* nomenclature. For each conformation, complete the Newman projection and draw the structure of the elimination product. Label all alkenes as *E* or *Z*. The two alkenes are not formed in equal amounts; write the words "major" and "minor" close to the appropriate product. In the box below, explain why one product is formed more than the other. Finally, state whether this reaction is stereospecific (stereoselective or stereospecific). (3 p. for "blanks", 8 p. for labels & structures, 3 p. for explanation)

Perspective Drawing  S	Newman Projection 	Elimination Product  Z
Perspective Drawing  S	Newman Projection 	Elimination Product  E

Explanation:

The *E*-isomer is the major product.

The conformation with the Me-Ph *gauche* interaction is less likely.

More product from the more stable conformation!

Question 7. Nucleophilic Substitution and Elimination III. (16 points)

PE2-Q2 What nucleophile is needed to prepare a thioether by way of an S_N2 reaction?

- a. RO^-
- b. RS^-**
- c. HS^-
- d. CN^-
- e. $RC\equiv C^-$

PE2-Q5 Which statement best describes the reaction order of the unimolecular nucleophilic substitution?

- a. First-order in alkyl halide, zero-order in nucleophile, zero-order overall
- b. First-order in alkyl halide, zero-order in nucleophile, first-order overall**
- c. First-order in alkyl halide, first-order in nucleophile, zero-order overall
- d. First-order in alkyl halide, zero-order in nucleophile, second-order overall
- e. Second-order in alkyl halide, zero-order in nucleophile, zero-order overall

PE1-Q5 How many β -carbons are there in 2-bromopropane and, if any, how many of these are secondary C-atoms?

- a. No β carbons
- b. 1 β carbon, 0 secondary β carbons.
- c. 2 β carbons, 0 secondary β carbons.**
- d. 2 β carbons, 1 secondary β carbons.
- e. 2 β carbons, 2 secondary β carbons.

PE1-Q8 The E2 reaction of 2-bromo-2-methylbutane gives mixtures of 2-methyl-2-butene and 2-methyl-1-butene. The ratio of these products depends on the choice of base employed. Which base gives the highest yield of 2-methyl-2-butene?

- a. $H_3C-H_2C-O^-$**
- b. $(H_3C)_2HC-O^-$
- c. $(H_3C)_3C-O^-$
- d. $(H_3C)_2(H_3C-H_2C)C-O^-$
- e. $(H_3C-H_2C)_3C-O^-$