

Chemistry 210
“Organic Chemistry I”
Summer Semester 1999
Dr. Somnath Sarkar

Final Examination

Thursday, July 29, 1999, 6:30– 8:30

Name:

Question 1 Stereochemistry(MC#1)	16	
Question 2. Substitution(MC #2)	16	
Question 3. Elimination(MC#3))	16	
Question 4. Alkynes (MC #4)	16	
Question 5. Structure and Synthesis of Alcohols(MC#5)	16	
Question 6. Reactions of Alcohols(MC #6)	16	
Question 7. Ring-flipping in Cyclohexane.	18	
Question 8: Nucleophilic substitution (News Item)	14	
Question 9: Mechanism of bromination of Alkene	24	
Question 10: Elimination	16	
Question 11: Synthesis of Alcohol	14	
Question 12: Reactions from alkene and alcohols	18	
Total	200	
Multiple Choice Points and Percentage:		

Look up the answers for the multiple choice questions on Dr. Glaser's Web page.

Question 1. Stereochemistry. (16 points)

E-Q8

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

E-Q22 Which of the following compounds is a *meso* compound?

- a. 1,1-dichlorocyclopropane
- b. *cis*-1,2-dichlorocyclopropane
- c. *trans*-1,2-dichlorocyclopropane
- d. *cis*-1-chloro-2-bromocyclopropane
- e. *trans*-1-chloro-2-bromocyclopropane

E-Q19 With two chiral centers present, we can realize stereoisomers that are (R,R), (S,S), (S,R), and (R,S). Which pair of these stereoisomers is a pair of diastereomers?

- a. (R,R) and (S,S)
- b. (S,R) and (R,S)
- c. (R,S) and (S,S)
- d. (R,S) and (S,R)
- e. this option is not used

E-Q24 You would like to resolve a mixture of enantiomers of an carboxylic acid. What strategy would you pursue?

- a. use enantiomerically pure amine to make enantiomeric salts
- b. use diastereomerically pure amine to make diastereomeric salts
- c. use enantiomerically pure amine to make diastereomeric salts
- d. use racemic amine to make diastereomeric salts
- e. use enantiomerically pure amine to make racemic salts

Question 2. Substitution Reactions (16 points)

E-Q5 Why do polar aprotic solvents increase the rates of SN2 reaction?

- a. Aprotic solvents solvate the nucleophile less, “naked” nucleophiles are more reactive
- b. Aprotic solvents always have low polarity
- c. Aprotic solvents better solvate the leaving group and therefore accelerate the reaction
- d. Aprotic solvents raise the energy of the reagents and therefore accelerate the reaction
- e. This option is not used.

E-Q6 Among the following solvents, which one is protic?

- a. Ethylacetate
- b. Acetone
- c. Acetic acid
- d. N,N-dimethylformamide, DMF
- e. Dimethyl sulfoxide, DMSO

E-Q10 Which type of substrate shows the highest reactivity in SN2 reaction?

- a. Methyl halide
- b. Primary alkyl halide
- c. Secondary alkyl halide
- d. Tertiary alkyl halide
- e. Quaternary alkyl halide

E-Q12 Which statement best describes the mechanism of SN2 reaction?

- a. Front-side attack with retention of configuration
- b. Front-side attack with inversion of configuration
- c. Back-side attack with retention of configuration
- d. Back-side attack with inversion of configuration
- e. Front- and back side attack with racemization

Question 3. Elimination (16 points)

- E-Q4 The E1 reaction of 3-chloro-2-methyl-2-phenylbutane yields 2-methyl-3-phenyl-2-butene in several steps. Which step does not belong in the sequence?
- Heterolytic C-Cl dissociation
 - Formation of a secondary carbenium ion
 - 1,2-methyl shift reaction
 - Formation of a tertiary benzylic cation
 - Loss of a hydride
- E-Q6 The E2 reaction is a 1,2-elimination of a proton H^+ and a leaving group Y^- . How many sigma bonds are there between the proton and the leaving group in the substrate?
- 1
 - 2
 - 3
 - 4
- E-Q11 Imagine the reaction coordinate diagram for the E2 reaction of 2-bromobutane. Which of the statement **does not** apply.
- There is one path leading to 1-butene and one path leading to 2-butene
 - The TS leading to 1-butene and 1-butene both are less stable than the TS leading to 2-butene and 2-butene respectively.
 - The transition states are alkene like
 - the CC double bond is formed more in the TS for the formation of the 2-butene than in the TS leading to 1-butene
 - 1-butene is formed first and then it is converted to 2-butene.
- E-Q13 The E2 reaction of 2-bromo-3-methyl-1-phenylbutane with hydroxide results in 3-methyl-1-phenyl-1-butene as the major product. Which one of the following statements explain the regiochemistry?
- 3-methyl-1-phenyl-1-butene is the expected Saytzeff product
 - 3-methyl-1-phenyl-1-butene is not the Saytzeff product because a small base was used
 - 3-methyl-1-phenyl-1-butene is the not the Saytzeff product and formed because the product can conjugate with a benzyl group
 - 3-methyl-1-phenyl-1-butene is not the Saytzeff product and formed because the product can conjugate with a phenyl group.

Question 4. Alkynes(16 points)

E-Q8 What base is best used to deprotonate acetylene?

- a. hydroxide, HO^-
- b. alkoxide, RO^-
- c. fluoride, F^-
- d. amide, NH_2^-
- e. chloride, Cl^-

E-Q17 In the presence of excess hydrogen bromide, what is the major product of the addition of HBr to 2-pentyne?

- a. 2-bromopentene
- b. 1-bromopentene
- c. 1,2-dibromopentene
- d. 2,2-dibromopentene
- e. 1,1-dibromopentene

E-Q20 What alkyne is the best starting material for the synthesis of the methylethylketone, $\text{H}_3\text{C-CO-CH}_2\text{-CH}_3$, via acid catalyzed hydration?

- a. ethyne
- b. propyne
- c. 1-butyne
- d. 2-butyne
- e. methylpropyne

E-Q27. What is the product of the reduction of 2-pentyne with sodium in liquid ammonia?

- a. *cis*-2-pentene
- b. *trans*-2-pentene
- c. *cis*-1-pentene
- d. *trans*-1-pentene
- e. *gauche*-2-pentene

Question 5. Structure and Synthesis of Alcohols (16 points)

E-Q1. What type of orbitals are occupied by the lone pairs in the alcohol group?

- a. Pure s-AO
- b. Pure p-AO
- c. sp-hybrids
- d. sp²-hybrids
- e. sp³-hybrids

E-Q3 Identify the tertiary alcohol among the following alcohol

- a. Cyclohexanol
- b. Phenol
- c. 2-methyl-2-propanol
- d. Hydroquinone
- e. Benzyl alcohol

E-Q6 In what types of positions will you find the hydroxyl groups in the most stable structure of *cis*-cyclohexenediglycol?

- a. Both axial
- b. Both equatorial
- c. One axial and one equatorial
- d. This option is not used
- e. This option is not used

E-Q15 Which statement best describes the polarity of the C-Li bond in an organolithium compound?

- a. The C-Li bond is highly covalent and not very polar.
- b. The C-Li bond is highly covalent and very polar, C positive, Li negative
- c. The C-Li bond is highly polar and almost ionic, C positive, Li negative
- d. The C-Li bond is highly covalent and very polar, C negative, Li positive
- e. The C-Li bond is highly polar and almost ionic, C negative, Li positive.

Question 6. Reactions of Alcohols (16 points)

E-Q1 Which one of the following statements **does not** describe an oxidation?

- a. Loss of hydrogen gas
- b. Addition of atomic oxygen
- c. Addition of molecular oxygen
- d. Addition of halogen atom or molecule
- e. Addition of a hydride ion

E-Q4 Which is the correct formula for sodium dichromate?

- a. $\text{Na}_2\text{Cr}_2\text{O}_5$
- b. $\text{Na}_2\text{Cr}_2\text{O}_6$
- c. $\text{Na}_2\text{Cr}_2\text{O}_7$
- d. NaCr_2O_6
- e. NaCr_2O_7

E-Q16. What is the molecular formula of thionyl chloride?

- a. SOCl
- b. SOCl_2
- c. SOCl_3
- d. SO_2Cl
- e. SO_2Cl_2

E-Q24. Phosphoric acid can form mono-, di- and triesters. Diesters of phosphoric acid are part of the backbone of RNA and DNA. Identify the molecular formula of the dimethylester of phosphoric acid.

- a. $\text{O}=\text{P}(\text{OH})_3$
- b. $\text{O}=\text{P}(\text{OH})_2(\text{OMe})$
- c. $\text{O}=\text{P}(\text{OH})(\text{OMe})_2$
- d. $\text{O}=\text{P}(\text{OMe})_3$
- e. This option is not used

Question 7a. Energy Profile for Ring Flipping in Cyclohexane. (14 points)

Draw an energy profile for the ring flipping in cyclohexane. Indicate which point(s) on the diagram correspond to “half-chair,” “twist-boat” and “boat” conformations (write appropriate word into diagram). Finally, draw Newman projections of the “chair” and “boat” conformations of cyclohexane.

12 point

Look up the conformational energy diagram and the structure for cyclohexane in your textbook, P. 113, Chapter 3, Wade, 4th Ed.

Newman projection of “chair”	Newman projection of “boat”
Look up the structure on P. 112, Chapter 3, in your textbook . Wade, 4th Ed.	

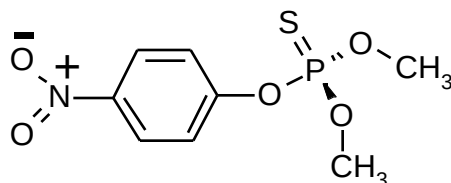
7b. Draw the most stable chair conformation for cis-1,2-dichlorocyclohexane. Perform a ring flip and draw the chair. Make sure that you show the bond movement of the chair clearly.

6 points

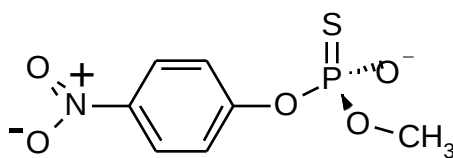
Look up the structure on page 120 in your textbook for cis-1,2-dimethylcyclohexane. In this questions those two methyl groups are changed to chloro. The answer is the same for chloro .

Look up AK for the 4th Exam from Dr. Glaser's W99 semester.

8. The article, "BAN IS SOUGHT ON PESTICIDES TO PROTECT KIDS" (*The Arizona Republic*, Jan. 29, **1998**) talked 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_N1 , S_N2) reaction can occur. This S_N reaction is facilitated by the fact that the nucleofuge is a good leaving group. (2 point)



- (a) Consider the reaction of methoxide ion (CH_3O^-) with methyl parathion. Draw the structure of the product of this reaction and draw the structure of the leaving group as well. (6 point)



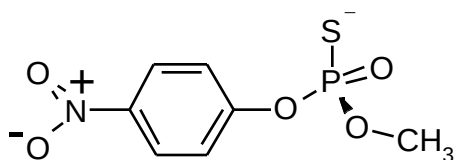
CH_3OCH_3

Structure of the product

Leaving group

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

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Resonance stabilized leaving group

Look up the AK for the 4th Exam(Q.2) from Dr. Glaser's Web page for W99.

9. Electrophilic addition of bromine. (24 points)

Let's look at the addition of Br_2 to propene. This reaction involves the electrophilic addition of a Br^+ to the $\text{C}=\text{C}$ bond of propene and a bridged ----- ion is formed. This intermediate is then attacked by a bromide ion. The Br^- can attack at the terminal or at the central C -atom but the attack at the ----- (central, terminal) position will be favored since this carbon carries a -----(smaller, larger) positive charge in the intermediate because it is ----- (more, less) substituted. In the end a 1,2-dibromopropane is formed that contains one $-\text{CH}_2\text{Br}$ group and one $-\text{CHBr}$ group. Now we note that the central carbon has become chiral as the result of the bromination. The ratio of R and S centers is however, exactly unity and the product is ----- . To fully realize the stereochemistry, complete the following questions.

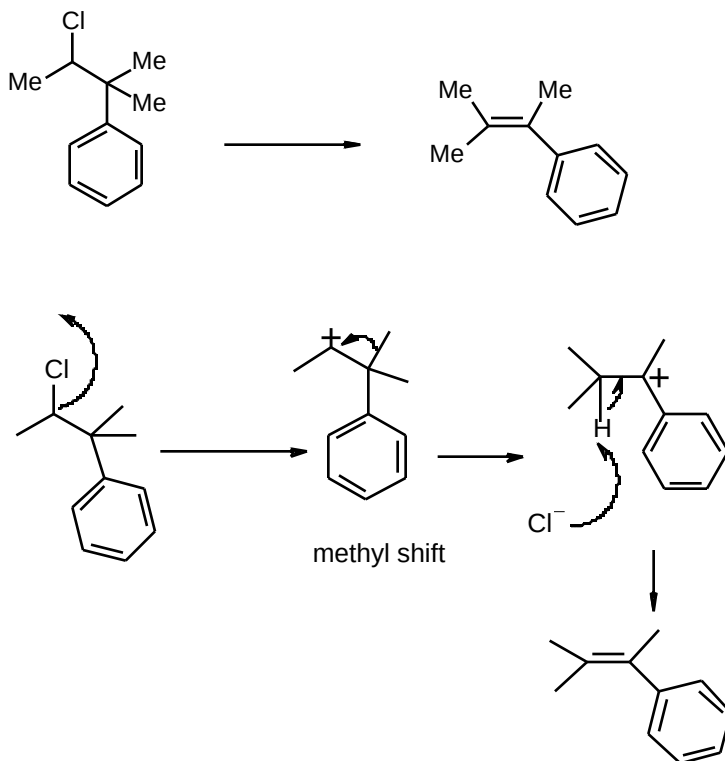


Propene

- a. Draw the intermediate formed by attack of Br^+ from the top and then draw the product formed from the trans addition of Br^- . Assign the stereochemistry with R or S.
- b. Draw the intermediate formed by the attack of Br^+ from the bottom and then draw the product formed by the trans addition of Br^- . Assign the stereochemistry.

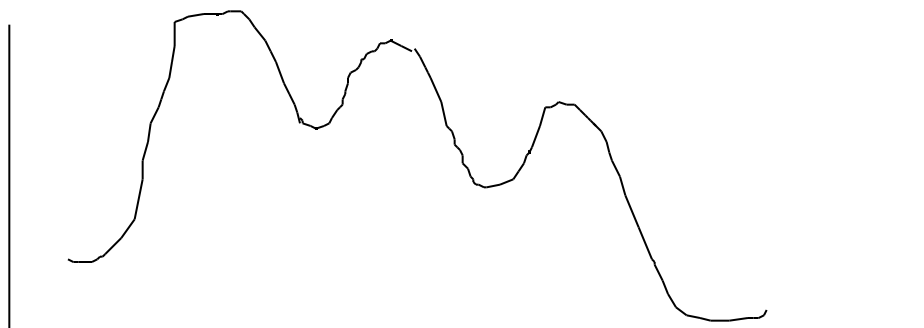
Q10. Elimination Reaction

The E1 reaction of 3-chloro-2-methyl-2-phenylbutane yields 2-methyl-3-phenyl-2-butene in several steps. Provide a mechanism for this reaction. Draw all the intermediates and use arrow-pushing to arrive at the product. Following is the reaction. All the hints to solve this problem is in the multiple choice question (**Question 3, EQ4**) **12 point**



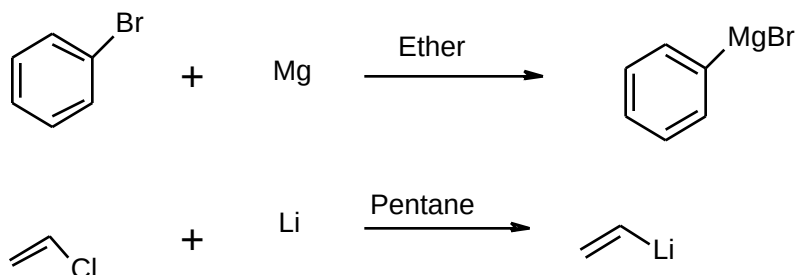
- b. How many intermediates and transition states are involved in this reaction? Draw an activation energy diagram indicating all the steps. **4 point**

Two intermediates and three transition states. Not a very good drawing, but it will give you the idea.

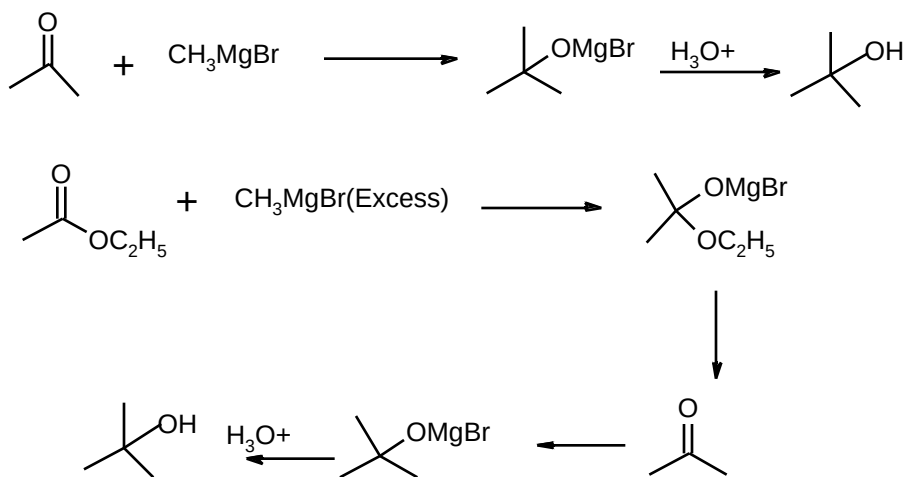


Q.11 Synthesis of alcohols with organometallics(12 points)

- a.** .Provide syntheses for phenylmagnesium bromide and vinyl lithium. In each case draw the structure of the starting materials and the product and specify the solvent. **6 points**



- b.** Suggest **two** synthetic routes to prepare tertiary butanol (2-Methyl-2-propanol) by using a Grignard reagent and a carbonyl compound of your choice. Draw starting material, all intermediates and products. **8 points**



Q12. Reactions of alkene and alcohols.

Provide the product with proper regiochemistry and stereochemistry for the following reactions.

18 points

