

Department of Chemistry  
SUNY/Oneonta

Chem 221 - Organic Chemistry I

Examination #4 - December 9, 2002

INSTRUCTIONS ---

This examination is in multiple choice format; the questions are in this Exam Booklet and the answers should be placed on the "Test Scoring Answer Sheet" which must be turned in and will be machine graded.

On the Test Scoring Answer Sheet, using a soft pencil, enter the following data (in the appropriate places): your name, instructor's name, your student (or Social Security) number, course number (30022101) and the test number (04). Darken the appropriate bubbles under the entries (do not darken a bubble under the letter in your student number), making dark black marks which fill the bubbles.

You may use a set of molecular models, but no other aids, during the exam.

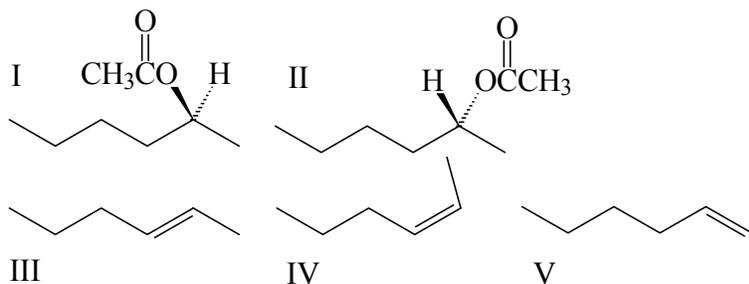
Answer all questions; they are worth 3.33 points each.

You have 50 minutes. Good luck!

In questions 1-5 select the mechanism(s) [there may be more than one] that fit(s) the description provided, from the list of mechanisms below. The substrate would be an alkyl halide or tosylate.

List of mechanisms: (A)  $S_N1$ , (B)  $S_N2$ , (C) E1, (D) E2, (E)  $S_N1$  &  $S_N2$ , (F) E1 & E2, (G)  $S_N1$  & E1, (H)  $S_N2$  & E2

- This reaction mechanism is characterized by inversion of stereochemistry at a stereogenic reaction center and exhibits second-order kinetics.
- This reaction mechanism is characterized by partial or complete racemization at a stereogenic reaction center and exhibits first-order kinetics.
- This reaction mechanism is characterized by a carbocation intermediate.
- This reaction mechanism is characterized by the requirement that the leaving group and a hydrogen on an adjacent carbon be periplanar and preferably anti-periplanar.
- These mechanisms will both operate if a  $2^\circ$  substrate is reacted with a high concentration of strong base/nucleophile.
- What would be the major product(s) that would form from reaction of (S)-2-bromohexane with acetate ion at room temperature if the reaction exhibits second order kinetics?



- (A) I, (B) II, (C) III, (D) IV, (E) V, (F) I&II; racemic mixture, (G) I&II; unequal amounts, (H) III, IV&V; III > IV > V, (I) III, IV&V; V > III > IV
- Rank the following substrates in order of decreasing reactivity in an  $S_N2$  reaction (most reactive first, least reactive last).  
 (I)  $(CH_3)_3C-Br$ , (II)  $CH_3Br$ , (III)  $CH_3CH_2Cl$ , (IV)  $CH_3CH_2Br$   
 (A) I > II > III > IV, (B) IV > I > II > III, (C) IV > III > II > I,  
 (D) I > IV > II > I, (E) II > IV > III > I

8. Rank the following substrates in order of decreasing reactivity in an  $S_N1$  reaction (most reactive first, least reactive last). [Note:  $C_6H_5$  represents the phenyl group, *ie* a benzene ring.]

(I)  $CH_3Br$ , (II)  $C_6H_5(CH_3)_2CBr$ , (III)  $(CH_3)_3CBr$ , (IV)  $(C_2H_5)_2CHBr$ , (V)  $C_2H_5Br$

(A)  $I > II > III > IV > V$ , (B)  $I > V > IV > III > II$ , (C)  $II > III > IV > V > I$   
 (D)  $II > III > IV > I > V$ , (E) None of the previous answers is correct.

9. In which of the solvents listed below would the following  $S_N2$  reaction be fastest?



(A) hexane, (B) methanol,  $CH_3OH$ , (C) diethyl ether,  $(C_2H_5)_2O$ , (D) acetonitrile,  $CH_3C\equiv N$

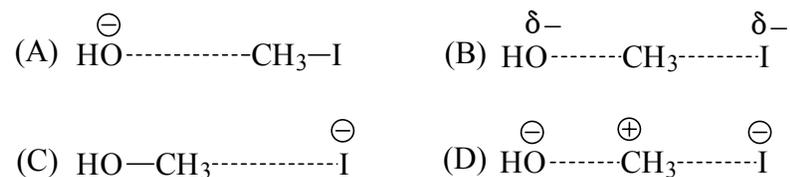
10. If a reaction proceeds through an  $S_N1$  mechanism and the concentrations of both the substrate and base are doubled, the reaction rate will

(A) remain the same. (B) double. (C) triple. (D) quadruple.  
 (E) None of the previous answers is correct

11.  $(CH_3)_3C-Br + H-C\equiv C^-Na^+ \longrightarrow$  major product(s)

(A)  $(CH_3)_3C-C\equiv C-H + NaBr$ , (B)  $(CH_3)_2C=CH_2 + H-C\equiv C-H + NaBr$ ,  
 (C)  $(CH_3)_3C^-Na^+ + H-C\equiv C-Br$ , (D) There would be no reaction.  
 (E) None of the above answers.

12. The structure of the transition state for the reaction of hydroxide ion with methyl iodide is best represented by



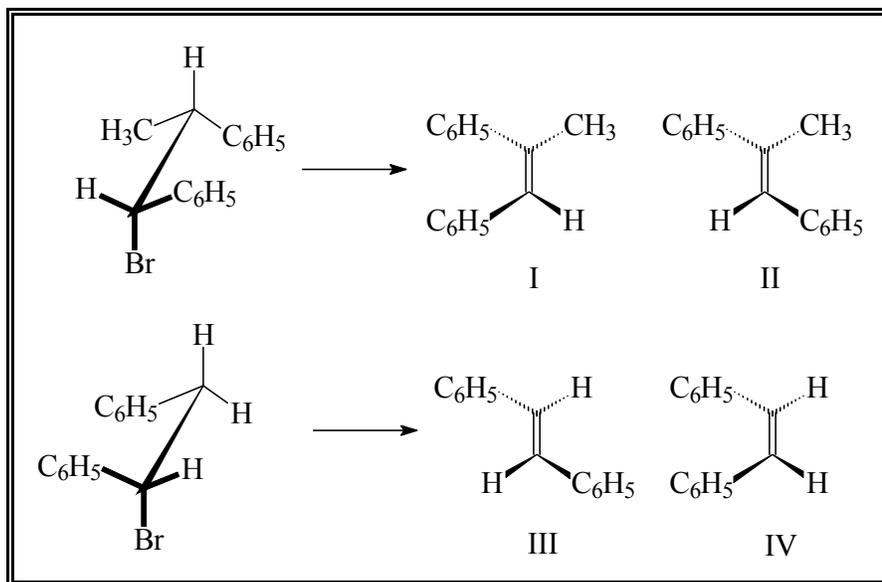
The following two questions consist of a statement followed by the connecting word **because** followed by a reason: <statement> **because** <reason>. In each question choose the correct description of the statement and the reason from the list below:

- (A) The statement and the reason are both factually true, and the reason is the correct explanation of the statement.  
 (B) The statement and the reason are both factually true, but the reason is not the correct explanation of the statement.  
 (C) The statement is true and the reason is false.  
 (D) The statement is false and the reason is true.  
 (E) Both the statement and reason are false.

13. Reaction of a bulky base such as  $(\text{CH}_3)_3\text{CO}^- \text{K}^+$  with secondary alkyl halides gives predominantly E2 elimination rather than  $\text{S}_{\text{N}}2$  substitution **because** the transition state for  $\text{S}_{\text{N}}2$  reaction is more sterically hindered than that for E2 reaction.

14.  $\text{S}_{\text{N}}2$  reactions of the type  $\text{RBr} + \text{NaOH} \rightarrow \text{ROH} + \text{Na}^+ \text{Br}^-$  generally go slower in a solvent like dimethyl sulfoxide (DMSO) than in a solvent like ethanol **because** dimethyl sulfoxide can solvate cations well but cannot solvate anions very well.

15. Consider the two E2 eliminations shown in the figure to the right. From the list of answers below, select the answer which best describes how much of each of the listed compounds, I-IV, would form.



- (a) I-IV would form in approximately equal amounts.
- (b) I-IV would form, but there would be more II than I and more III than IV.
- (c) I would form but not II. III and IV would form, with more III than IV.
- (d) I would form but not II. III and IV would form, with more IV than III.
- (e) II would form but not I. III and IV would form, with more III than IV.
- (f) II would form but not I. III and IV would form, with more IV than III.
- (g) I and II would form, with more I than II. III would form but not IV.
- (h) I and II would form, with more II than I. III would form but not IV.
- (i) I and II would form, with more I than II. IV would form but not III.
- (j) I and II would form, with more II than I. IV would form but not III.

16. In an NMR spectrum, signals arising from hydrogens and carbons that are near an electronegative element are moved

(A) upfield. (B) downfield. (C) to the outfield. (D) to the infield. (E) to "The Field of Dreams."

17. The NMR signal from a proton that has three proton neighbors, equivalent to each other but different from itself, will be split into a

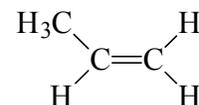
(A) doublet. (B) triplet. (C) quartet. (D) quintet. (E) sextet.

18. How many signals would the compound to the right give in a  $^{13}\text{C}$  NMR spectrum?



(A) 1, (B) 2, (C) 3, (D) 4, (E) 5

19. How many signals would the compound to the right give in a proton NMR spectrum?



(A) 2, (B) 3, (C) 4, (D) 5, (E) 6

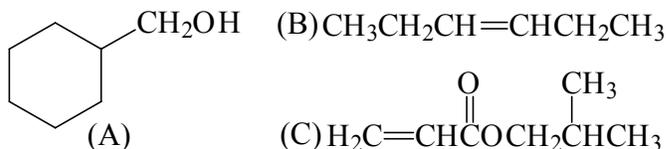
For questions 20-21 consider the following compound:



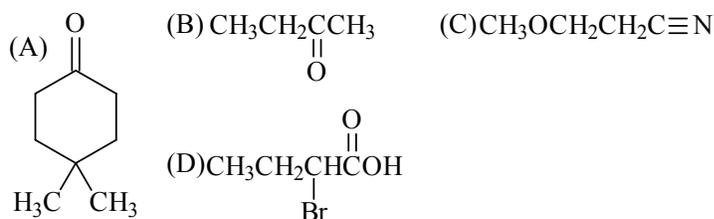
20. How many signals will appear in the proton NMR of this compound?

(A) 1, (B) 2, (C) 3, (D) 4, (E) 5, (F) 8

21. Which protons would appear furthest downfield?  
 (A) CH<sub>3</sub> on left, (B) CH<sub>2</sub>, (C) CH<sub>3</sub> on right.
22. Match the broadband decoupled carbon-13 NMR data given below with one of the structures also shown below: Signals at the following  $\delta$  values (ppm downfield from TMS): 19.1, 28.0, 70.5, 129.0, 129.8, 165.8.

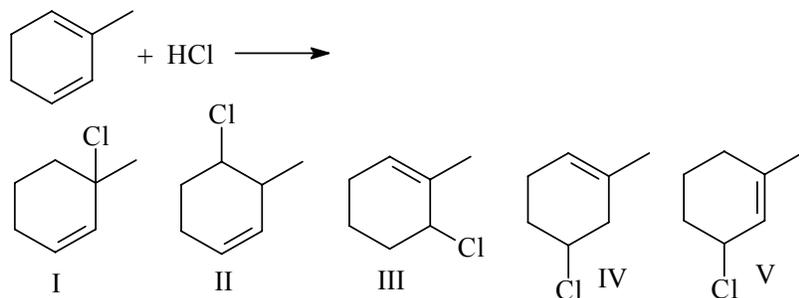


In questions 23-25 match the proton NMR data given in the question with one of the structures shown below:

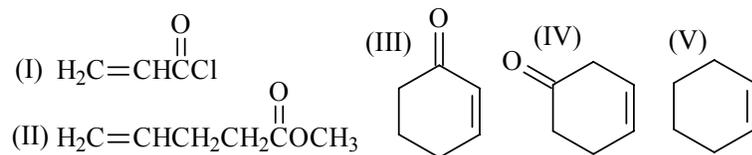


23. Signals at the following  $\delta$  values (ppm downfield from TMS): 1.08(triplet), 2.07(quintet), 4.23(triplet), 10.97(singlet).
24. Signals at the following  $\delta$  values (ppm downfield from TMS): 1.05(triplet), 2.13(singlet), 2.47(quartet).
25. Signals at the following  $\delta$  values (ppm downfield from TMS): 2.62(triplet), 3.40(singlet), 3.62(triplet).
26. Rank the following dienes in order of decreasing stability (most stable first).  
 (I) H<sub>2</sub>C=C=CH<sub>2</sub> (II) H<sub>2</sub>C=CH-CH<sub>2</sub>-CH=CH<sub>2</sub>  
 (III) CH<sub>3</sub>CH=CH-CH=CHCH<sub>3</sub> (IV) H<sub>2</sub>C=CH-CH=CH<sub>2</sub>  
 (A) I>II>III>IV, (B) IV>III>II>I, (C) III>IV>II>I, (D) II>III>IV>I

27. Which of the following compounds would be formed in significant quantity in this reaction?



- (A) I, II, III, (B) III, IV, V, (C) I, III, V, (D) II, IV
28. If a reaction can proceed both under kinetic control and thermodynamic control to give different products and in a given situation it proceeds under thermodynamic control it will be the case that
- (A) the product that forms faster will be the major one.  
 (B) the product that is most stable will be the major one.  
 (C) the product that is least stable will be the major one.
29. Which of the following alkenes would be good dienophiles in a Diels-Alder reaction?



- (A) I, II, (B) III, IV, V, (C) I, III, (D) II, IV, (E) V

30. In the laboratory this semester you synthesized, or attempted to synthesize, *endo*-norbornene-5,6-dicarboxylic anhydride by reacting 1,3-cyclopentadiene with maleic anhydride in a Diels-Alder reaction. Which of the compounds shown is *endo*-norbornene-5,6-dicarboxylic anhydride?

