

Department of Chemistry  
SUNY/Oneonta

Chem 221 - Organic Chemistry I

Examination #4 - December 9, 2002 **ANSWERS**

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!

**Answers are highlighted in red.**

Explanations are in red type.

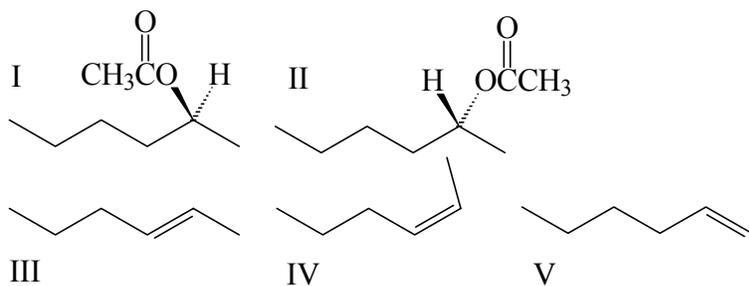
In questions 1-5 select the mechanism(s) [there may be more than one] that fit(s) the description provided, from the list of mechanisms below. The substrate would be an alkyl halide or tosylate.

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. **(B)**
- This reaction mechanism is characterized by partial or complete racemization at a stereogenic reaction center and exhibits first-order kinetics. **(A)**
- This reaction mechanism is characterized by a carbocation intermediate. **(G)**
- 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. **(D)**
- These mechanisms will both operate if a  $2^\circ$  substrate is reacted with a high concentration of strong base/nucleophile. **(H)**

Secondary substrates can react by  $S_N1$ , E1,  $S_N2$ , and E2 mechanisms. The rates of the  $S_N1$  and E1 mechanisms are, for the most part, unaffected by base/nucleophile aggressiveness or concentration. Their rates depend on how fast the substrate forms a carbocation and the base/nucleophile is not involved in this rate limiting step. On the other hand, the rates of the  $S_N2$  and E2 mechanisms will be increased by higher concentrations of base/nucleophile and by a more aggressive base/nucleophile because the base/nucleophile is involved in the rate limiting step. So, in the presence of a high concentration of a strong base/nucleophile the  $S_N2$  and E2 mechanisms are speeded up, but the  $S_N1$  and E1 are not and, so, for the most part lose out.

- 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

$S_N2$  means inversion of configuration at the site of attack on the substrate.

7. 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 Steric effect.

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.

The rate depends on how fast the carbocation is formed; the more stable the carbocation the faster it is formed. There are two  $3^\circ$  carbocations here: II and III. II is more stable because it is also benzylic and is, therefore, resonance stabilized.

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,  $CH_3C\equiv N$

Solvents with negative ends solvate cations and leave anions less encumbered and more nucleophilic.

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

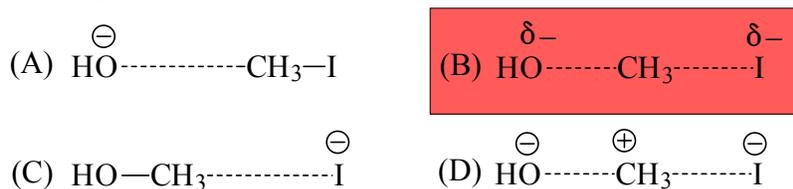
$S_N1$  rate =  $k_1[\text{substrate}]$ ; nucleophile/base concentration doesn't affect rate.

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

- (A)  $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{H} + \text{NaBr}$ , (B)  $(\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{H}-\text{C}\equiv\text{C}-\text{H} + \text{NaBr}$ ,  
 (C)  $(\text{CH}_3)_3\text{C}^-\text{Na}^+ + \text{H}-\text{C}\equiv\text{C}-\text{Br}$ , (D) There would be no reaction.  
 (E) None of the above answers.

(A), the substitution, only works well for  $1^\circ$  substrates. A  $3^\circ$  substrate will undergo elimination with a strong base/nucleophile like acetylide anion.

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

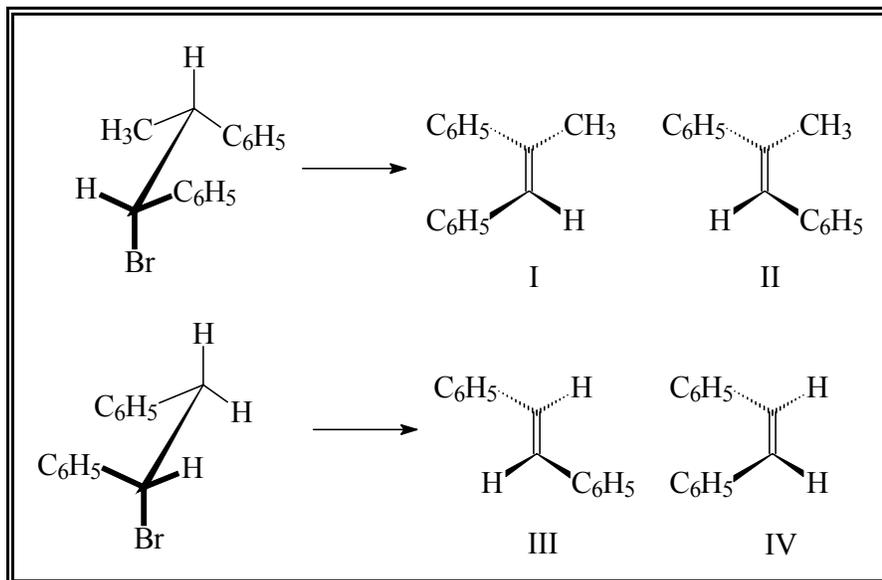


The following two questions consist of a statement followed by the connecting word **because** followed by a reason: <statement> **because** <reason>. In each question choose the correct description of the statement and the reason from the list below:

- (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. (A)

14.  $S_N2$  reactions of the type  $RBr + NaOH \rightarrow ROH + Na^+ Br^-$  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. **(D)**

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.

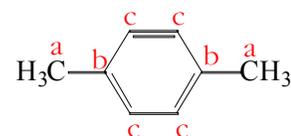
(i) I and II would form, with more I than II. IV would form but not III.

(j) I and II would form, with more II than I. IV would form but not III.

In the first reaction, the conformation shown is the only one that will react because in E2 the H and leaving group (Br) should be anti-periplanar. This gives I but not II. In the second reaction the conformation of the reactant shown will lead to IV, the phenyl groups cis to each other. However, there is a second conformation that can react in this case – the one obtained by rotating the rear group counterclockwise  $120^\circ$ . This conformation also has an H and the Br anti-periplanar and is more stable than the conformation shown because the bulky phenyl groups are also anti-periplanar to each other. [In the conformation shown, the bulky phenyl groups are syn-clinal to each other and there would be unfavorable steric interaction.] More molecules are in the conformation with the phenyl groups anti-periplanar than in the one shown. This conformation leads to III which is formed in greater quantity.

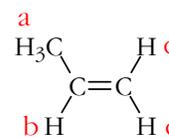
16. In an NMR spectrum, signals arising from hydrogens and carbons that are near an electronegative element are moved
- (A) upfield. (B) downfield. (C) to the outfield. (D) to the infield. (E) to "The Field of Dreams."
17. The NMR signal from a proton that has three proton neighbors, equivalent to each 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?



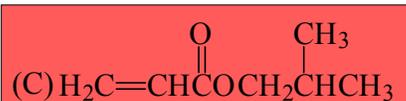
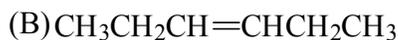
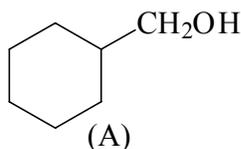
- (A) 2, (B) 3, (C) 4, (D) 5, (E) 6

For questions 20-21 consider the following compound:

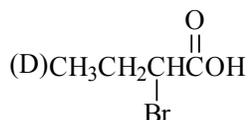
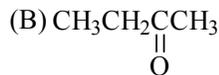
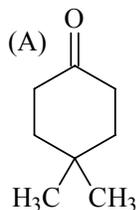


20. How many signals will appear in the proton NMR of this compound?
- (A) 1, (B) 2, (C) 3, (D) 4, (E) 5, (F) 8
21. Which protons would appear furthest downfield?
- (A)  $\text{CH}_3$  on left, (B)  $\text{CH}_2$ , (C)  $\text{CH}_3$  on right.

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. **Six signals means six different "kinds" of carbon. (A) has 5 and (B) has 3; only (C) has 6.**



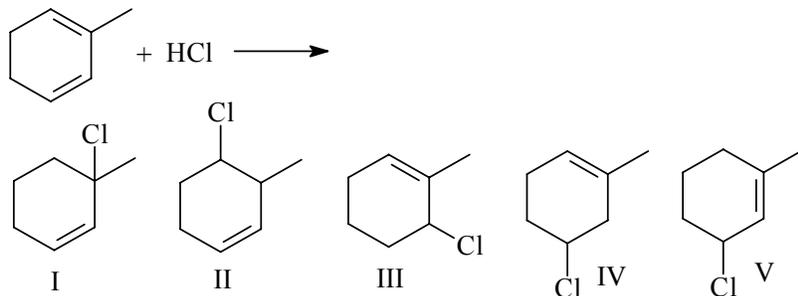
In questions 23-25 match the proton NMR data given in the question with one of the structures shown below:



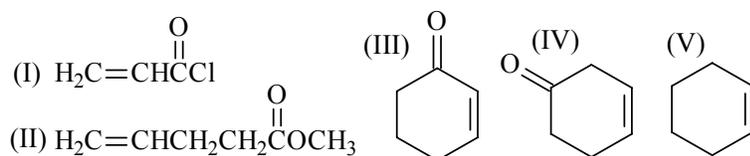
23. Signals at the following  $\delta$  values (ppm downfield from TMS): 1.08(triplet), 2.07(quintet), 4.23(triplet), 10.97(singlet). **(D) A, B, and C would each give 3 signals, not 4. The singlet at 10.97 is from a carboxylic acid proton and the splitting is consistent.**
24. Signals at the following  $\delta$  values (ppm downfield from TMS): 1.05(triplet), 2.13(singlet), 2.47(quartet). **(B) A, B, and C all have methyl groups that would produce a singlet, but only B has an ethyl group that would produce the triplet/quartet pattern.**
25. Signals at the following  $\delta$  values (ppm downfield from TMS): 2.62(triplet), 3.40(singlet), 3.62(triplet). **(C) The triplet/triplet pattern here comes from the isolated  $-\text{CH}_2-\text{CH}_2-$  group. None of the other compounds has this.**
26. Rank the following dienes in order of decreasing stability (most stable first).  
 (I)  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$  (II)  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$   
 (III)  $\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CHCH}_3$  (IV)  $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$   
 (A) I>II>III>IV, (B) IV>III>II>I, **(C) III>IV>II>I**, (D) II>III>IV>I

III and IV are both conjugated dienes, but III is more highly substituted. Cumulated dienes (I) are known to be less stable than conjugated or isolated (II) dienes.

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



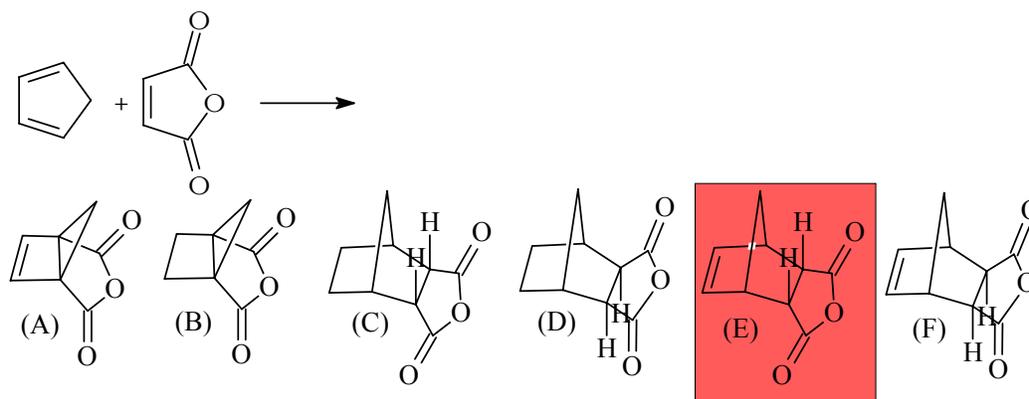
- (A) I, II, III, (B) III, IV, V, (C) I, III, V, (D) II, IV Resulting from both 1,2- and 1,4-addition to the conjugated diene with H attacking both the top and bottom carbons.
28. If a reaction can proceed both under kinetic control and thermodynamic control to give different products and in a given situation it proceeds under thermodynamic control it will be the case that
- (A) the product that forms faster will be the major one. Kinetic control.  
 (B) the product that is most stable will be the major one. Thermodynamic control.  
 (C) the product that is least stable will be the major one. Can happen with kinetic control.
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

Electron withdrawing groups adjacent to the double bond are helpful.

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?



E and F are the possible Diels-Alder products. They are diastereomers and very little of the *exo* product (F) forms – the Alder-Stein rule.