

Department of Chemistry & Biochemistry  
SUNY/Oneonta

Chem 221 - Organic Chemistry I

Examination #4 - December 6, 2004

**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.

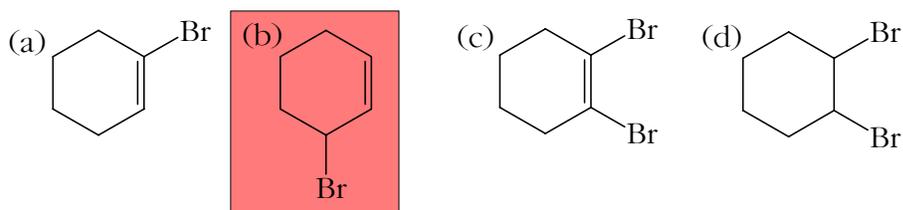
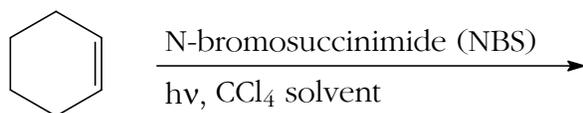
On the Test Scoring Answer Sheet, using a soft pencil, enter the following data (in the appropriate places):  
your name,  
your OSC student (NOT Social Security) number,  
and course number (30022101);  
darken the appropriate bubbles under the entries, making dark black marks which fill the bubbles.

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

Answer all questions; they are worth 3.79 points each.

You have 50 minutes. Good luck!

1. Select the principal product of the following reaction.

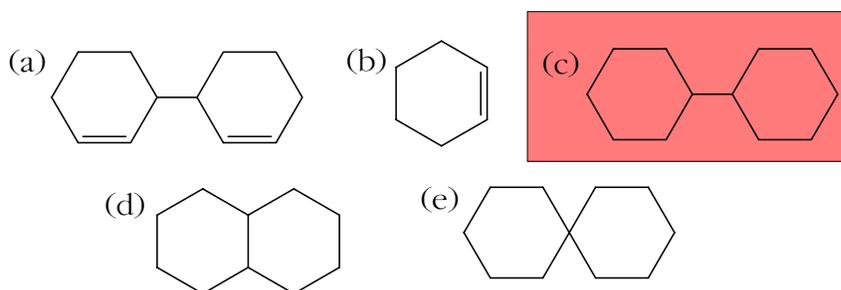
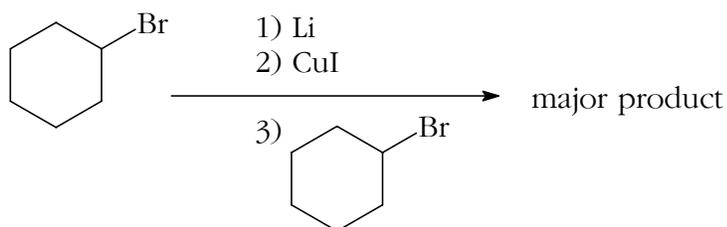


Allylic free radical bromination.

2. Rank the following free radicals in order to decreasing stability (most stable first).

(a) vinylic>methyl>primary>secondary>tertiary>allylic,  
(b) allylic>tertiary>secondary>primary>methyl>vinylic,  
(c) allylic>methyl>primary>secondary>tertiary>vinylic,  
(d) tertiary>secondary>primary>allylic>vinylic>methyl

3. What will be the major product which results from the following series of reactions?

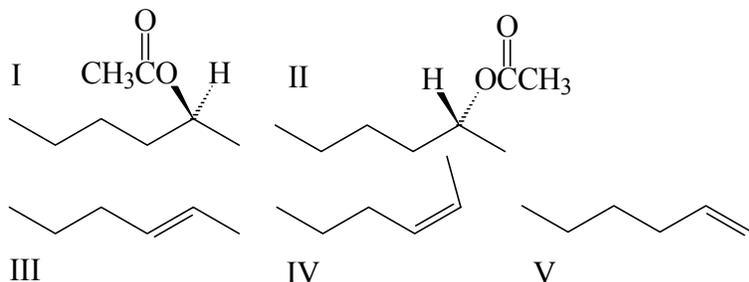


In questions 4-10 select the mechanism(s) [there may be more than one] that fit the description provided, from the list of mechanisms below. The substrate would be an alkyl halide or alkyl tosylate.

List of mechanisms: (a) S<sub>N</sub>1, (b) S<sub>N</sub>2, (c) E1, (d) E2, (e) S<sub>N</sub>1 & S<sub>N</sub>2, (f) E1 & E2, (g) S<sub>N</sub>1 & E1, (h) S<sub>N</sub>2 & E2

4. This reaction mechanism is characterized by inversion of stereochemistry at a stereogenic reaction center and exhibits second-order kinetics. (b)
5. This reaction mechanism is characterized by partial or complete racemization at a stereogenic reaction center and exhibits first-order kinetics. (a)
6. This reaction mechanism is characterized by a carbocation intermediate. (g)
7. This reaction mechanism is characterized by the requirement that the leaving group and a hydrogen on an adjacent carbon be coplanar and preferably anti-coplanar. (d)
8. This reaction mechanism is favored by 3° substrates, high temperatures, and a strong base. (d) Tertiary substrates favor S<sub>N</sub>1, E1, and E2. High temperatures favor elimination over substitution. A strong base or strong nucleophile will not speed up S<sub>N</sub>1 or E1, since the base or nucleophile is not involved in the rate limiting step in these mechanisms, but will speed up an E2 mechanism where the base is involved in the rate limiting step.
9. This reaction mechanism is favored by 3° substrates, low temperatures, polar solvents, and low concentrations of very weak bases. (a) Tertiary substrates favor S<sub>N</sub>1, E1, and E2. Low temperatures favor substitution (S) over elimination (E). High concentrations of strong bases would favor E2; low base concentrations favor S<sub>N</sub>1 and E1. If the base is very weak it is more likely to act as nucleophile (S<sub>N</sub>1) than it is to act as a base (E1).
10. These mechanisms will both operate if a 2° substrate is reacted with a high concentration of strong base/nucleophile. (h)
11. Which of the following mechanism types is(are) likely in this reaction:  
 $\text{CH}_3\text{I} + \text{KOH} \rightarrow \text{CH}_3\text{OH} + \text{KI}$   
(I) S<sub>N</sub>1, (II) S<sub>N</sub>2, (III) E1, (IV) E2  
(a) I&II, (b) III&IV, (c) I, (d) II

12. What would be the major product(s) that would form from reaction of (S)-2-bromohexane with acetate ion ( $\text{CH}_3\text{COO}^-$ ) 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
13. Rank the following substrates in order of decreasing reactivity in an  $\text{S}_{\text{N}}2$  reaction (most reactive first, least reactive last).

(I)  $(\text{CH}_3)_3\text{C-Br}$ , (II)  $\text{CH}_3\text{Br}$ , (III)  $\text{CH}_3\text{CH}_2\text{Cl}$ , (IV)  $\text{CH}_3\text{CH}_2\text{Br}$

(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

14. In which of the solvents listed below would the following  $\text{S}_{\text{N}}2$  reaction be fastest?



(a) hexane, (b) methanol,  $\text{CH}_3\text{OH}$ , (c) diethyl ether,  $(\text{C}_2\text{H}_5)_2\text{O}$ , (d) acetonitrile,  $\text{CH}_3\text{C}\equiv\text{N}$   
 Aprotic polar solvents speed up  $\text{S}_{\text{N}}2$  reactions.

15. If a reaction proceeds through an  $\text{S}_{\text{N}}1$  mechanism and the concentrations of both the substrate and nucleophile are doubled, the reaction rate will

(a) remain the same. (b) double. (c) triple. (d) quadruple.  
 (e) None of the previous answers is correct

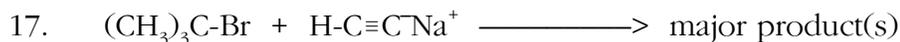
In  $\text{S}_{\text{N}}1$  the concentration of the nucleophile does not affect the rate.

16. For the following reaction carried out in aqueous ethanol, select the more reactive nucleophile in each pair:  $\text{CH}_3\text{Br} + \text{Nu}^- \rightarrow \text{CH}_3\text{-Nu} + \text{Br}^-$

Nucleophiles

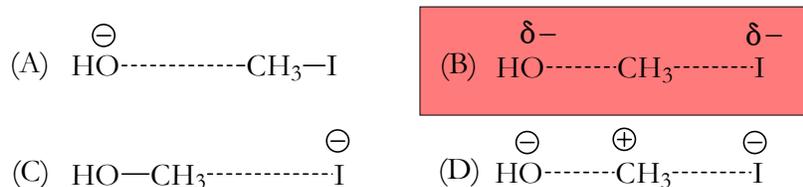
First pair:  $\text{I}^-$  and  $\text{Cl}^-$ . Second pair:  $\text{HS}^-$  and  $\text{H}_2\text{S}$ .

(a)  $\text{I}^-$  &  $\text{HS}^-$ , (b)  $\text{Cl}^-$  &  $\text{H}_2\text{S}$ , (c)  $\text{I}^-$  &  $\text{H}_2\text{S}$ , (d)  $\text{Cl}^-$  &  $\text{HS}^-$

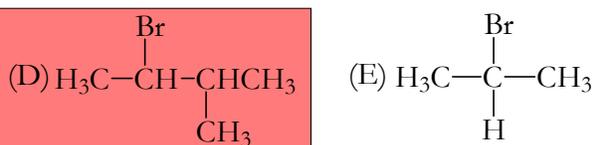
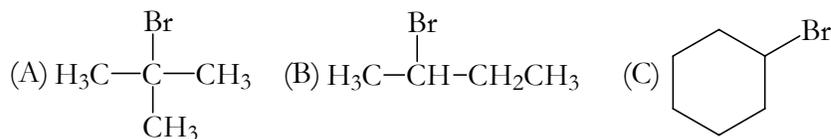


- (a)  $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{H} + \text{NaBr}$ , (b)  $(\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{H}-\text{C}\equiv\text{C}-\text{H} + \text{NaBr}$ ,  
 (c)  $(\text{CH}_3)_3\text{C}^- \text{Na}^+ + \text{H}-\text{C}\equiv\text{C}-\text{Br}$ , (d) There would be no reaction.  
 (e) None of the above answers.

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



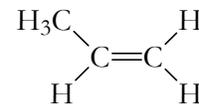
19. Which of the alkyl halides shown below would be most likely to give a rearranged product on solvolysis (reaction with solvent acting as nucleophile) in aqueous ethanol?



Water and ethanol are weak nucleophiles but make for a very polar solvent.  $\text{S}_{\text{N}}1$  is favored by polar protic solvents like ethanol and water.  $\text{S}_{\text{N}}1$  involves carbocations which can rearrange to form more stable carbocations.  $\text{S}_{\text{N}}2$  does not usually involve rearrangements; the nucleophile becomes attached to the same carbon as the leaving group. So, we are talking about an  $\text{S}_{\text{N}}1$  mechanism which is possible for secondary and tertiary substrates – all of the substrates listed. A rearrangement will only occur if a less stable carbocation is able to rearrange to a more stable carbocation. (D) is the only compound where this is possible: the secondary carbocation formed by ionization of the alkyl bromide can rearrange to a tertiary carbocation by a hydride shift involving the hydrogen on the carbon to the right of the positively charged carbon.

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.
20. 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)
21.  $\text{S}_{\text{N}}2$  reactions of the type  $\text{RBr} + \text{Na}^+ \text{OH}^- \rightarrow \text{ROH} + \text{Na}^+ \text{Br}^-$  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. (d)
22. Which of the following nuclei does *not* have a magnetic moment, and is, therefore, not NMR active?  
(a)  $^1\text{H}$ , (b)  $^{12}\text{C}$ , (c)  $^{13}\text{C}$ , (d)  $^{19}\text{F}$
23. 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.
24. 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, (f) 6, (g) 7, (h) 8
25. 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

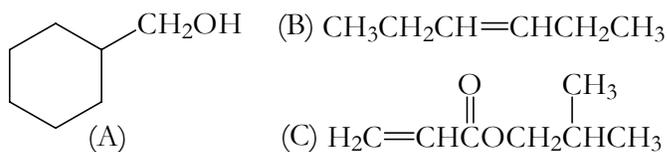


For questions 26-27 consider the following compound:  $\text{H}_3\text{C}-\text{O}-\text{CH}_2-\text{O}-\text{CH}_3$

26. How many signals will appear in the proton NMR of this compound?  
(a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 8
27. Which protons would appear furthest downfield?

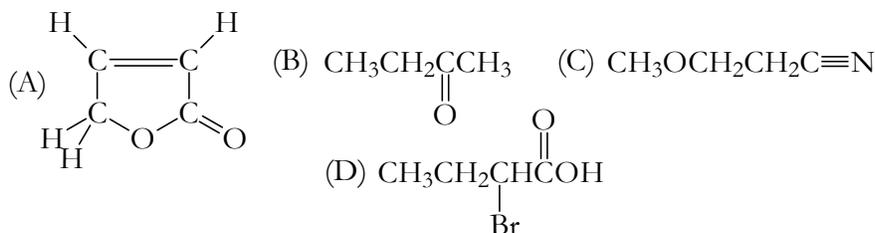
(a) CH<sub>3</sub> on left, (b) CH<sub>2</sub>, (c) CH<sub>3</sub> on right.

In questions 28-30 match the broadband decoupled carbon-13 NMR data given in the question with one of the structures shown below:



28. Signals at the following  $\delta$  values (ppm downfield from TMS): 68.2, 40.5, 29.9, 26.1, 26.9.  
**(A)**
29. Signals at the following  $\delta$  values (ppm downfield from TMS): 132, 27, 16.  
**(B)**
30. Signals at the following  $\delta$  values (ppm downfield from TMS): 19.1, 28.0, 70.5, 129.0, 129.8, 165.8.  
**(C)**

In questions 31-33 match the proton NMR data given in the question with one of the structures shown below:



31. Signals at the following  $\delta$  values (ppm downfield from TMS): 1.08(triplet), 2.07(quintet), 4.23(triplet), 10.97(singlet).  
**(D)**
32. Signals at the following  $\delta$  values (ppm downfield from TMS): 1.05(triplet), 2.13(singlet), 2.47(quartet).  
**(B)**
33. Signals at the following  $\delta$  values (ppm downfield from TMS): 2.62(triplet), 3.40(singlet), 3.62(triplet).  
**(C)**