Name _____

Department of Chemistry
SUNY/Oneonta

Chem 221 - Organic Chemistry I

Examination #3 - November 13, 2000

INSTRUCTIONS —

This examination has two parts. The first part 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.

The second part requires your responding to questions in the Exam Booklet by writing answers into the spaces provided. The Exam Booklet must be handed in and will be returned to you with a grade.

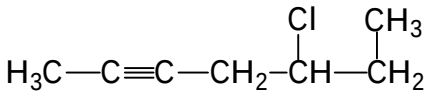
On the Test Scoring Answer Sheet, using a soft pencil, enter the following data (in the appropriate places): your name, instructor's name, your student (Social Security) number, course number (30022101) and the test number (03); darken the appropriate bubbles under the entries, making dark black marks which fill the bubbles.

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

Answer all questions. The questions on Part I are worth 2.5 points each.

You have 90 minutes. Good luck!

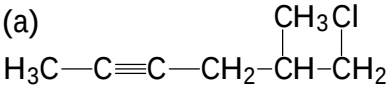
1. Select the correct IUPAC name for the compound shown to the right.



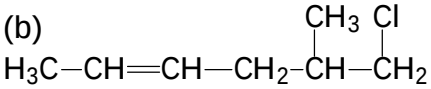
(a) 5-chloro-6-methyl-2-hexyne,
(b) 2-chloro-1-methyl-4-hexyne,
(c) 5-chloro-2-heptyne,
(d) 5-chloro-6-methyl-2-hexene,
(e) None of the above answers is correct.

2. Select the compound which is <u>not</u> isomeric with the others.

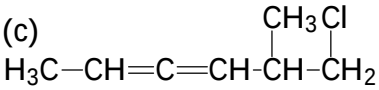
(a)



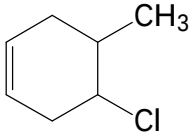
(b)



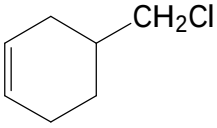
(c)



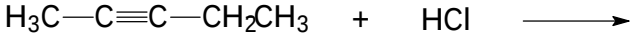
(d)



(e)



3. Select the answer which best describes the product(s) of the following reaction.

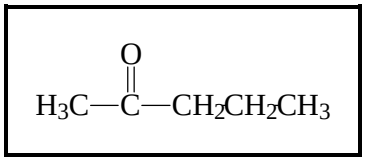


(I) $H_3C{-}CH{=}CCl{-}CH_2CH_3$ (II) $H_3C{-}CCl{=}CH{-}CH_2CH_3$

(III) $H_3C{-}CCl{=}CCl{-}CH_2CH_3$

(a) I, (b) II, (c) III, (d) I & II, in approximately equal quantity,
(e) I & II, but considerably more I than II,
(f) I & II, but considerably more II than I,
(g) I, II, & III, but mostly III.

4. Which compound would you start with to prepare 2-pentanone?

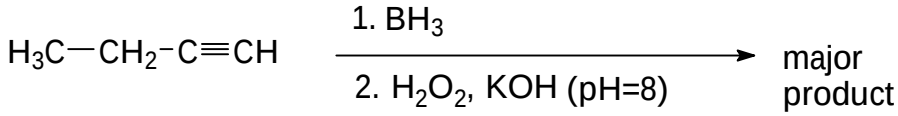


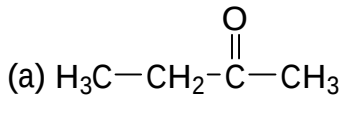
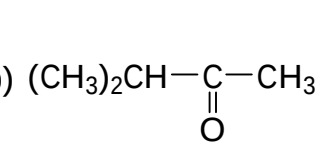
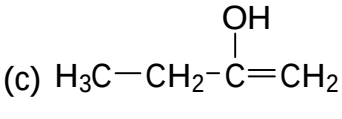
2-pentanone

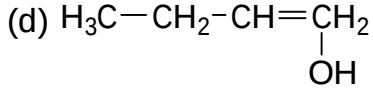
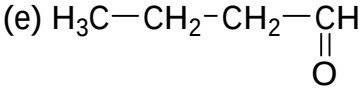
(a) $HC{\equiv}C{-}CH_2CH_2CH_3$ (b) $H_3C{-}C{\equiv}C{-}CH_2CH_3$

(c) $H_2C{=}CH{-}CH_2CH_2CH_3$ (d) $H_3C{-}CH{=}CH{-}CH_2CH_3$

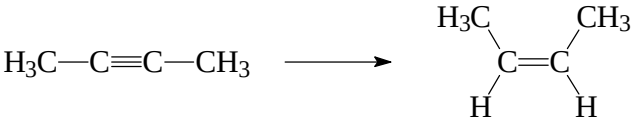
5. Select the principal product of the following reaction sequence.



(a) 
(b) 
(c) 

(d) 
(e) 

6. Select the appropriate reagents to carry out the following reaction.



(a) H_2, Lindlar catalyst, (b) H_2, Pt, (c) H_2O, H_2SO_4, $HgSO_4$, (d) Li, NH_3,
(e) $NaNH_2$ in NH_3

7. For which of the following reactions would K_{eq} be less than 1?
[pK_as: H_2O = 16, $CH_3C{\equiv}C{-}H$ = 25, NH_3 = 35]

I: $CH_3C{\equiv}C{-}H + NaNH_2 \rightleftharpoons CH_3C{\equiv}C{:}^- Na^+ + NH_3$

II: $CH_3C{\equiv}C{-}H + NaOH \rightleftharpoons CH_3C{\equiv}C{:}^- Na^+ + H_2O$

(a) I, (b) II, (c) I&II, (d) neither I nor II

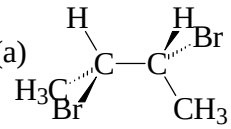
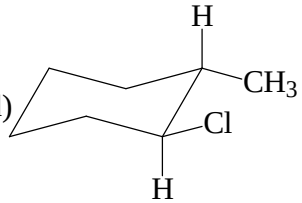
8. Which of the alkyl chlorides below is likely to be most successful in the following reaction, where R is an alkyl group: $CH_3C{\equiv}C{:}^-\ Na^+ + R\text{-}Cl \rightarrow CH_3C{\equiv}C\text{-}R + Na^+Cl^-$

(a) CH_3CH_2Cl, (b) $(CH_3)_3CCl$, (c) $(CH_3)_2CHCl$
(d) Bogus question, dude! Like, none of these compounds will react this way.

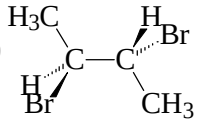
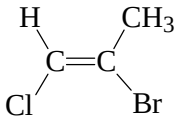
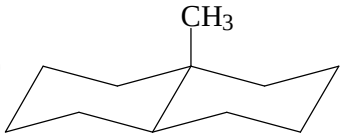
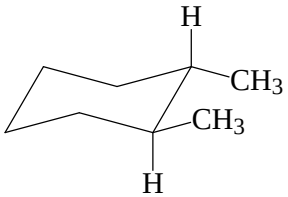
9. Your first assignment as junior chemist at the Carbonaceous Chemical Corporation is to make (±)-3,4-dibromohexane from 3-hexyne. Which of the following routes would be most successful?

(a) 1. H_2, Lindlar catalyst, 2. 1 equivalent Br_2 in CCl_4, (b) 1. 1 equivalent Br_2 in CCl_4, 2. BH_3, 3. H_2O_2, KOH, (c) 1. Li, NH_3, 2. H_2O, 3. Br_2 in CCl_4, (d) 2 equivalents HBr.

10. Which of the following molecules is achiral ?

(a) 
(b) $CH_3CHBrCl$ (c) CH_3CH_2Br (d) 

11. Which of the following molecules is chiral ?

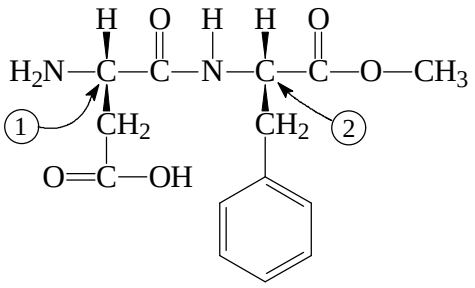
(a) 
(b) 
(c) 
(d) 

12. A meso structure is one which

(a) has chiral (stereogenic) centers and is chiral. (b) has chiral centers and is achiral.
(c) has no chiral centers and is chiral. (d) has no chiral centers and is achiral.

13. Which of the molecules shown in question #11 is a meso structure?

14. The structure of aspartame (G.D. Searle's Nutrasweet®) is shown to the right. How many different stereoisomers are possible for this structure, including the one shown?



(a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6

15. Indicate the absolute configuration of the two chiral centers in aspartame (question #14).

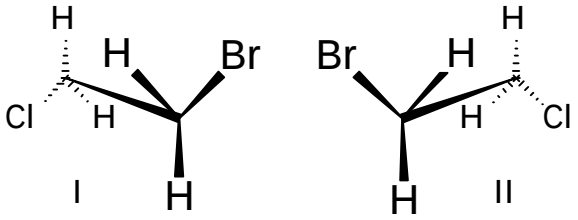
(a) 1: R, 2: R, (b) 1: S, 2: S, (c) 1: S, 2: R,
(d) 1: R, 2: S.

16. Which of the following is (are) always true about a compound which has only one chiral center, the configuration of which is R.

I: It is dextrorotatory (+ rotation of light). II: It is levorotatory (- rotation of light).
III: Its mirror image has the S configuration.

(a) I, (b) II, (c) III, (d) I&III, (e) II & III

17. What is the relationship between the two structures shown below?



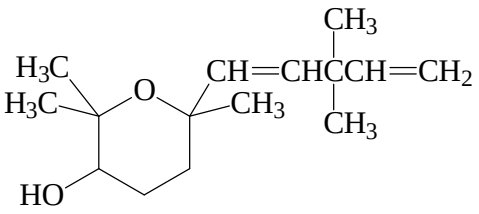
They are
(a) configurational enantiomers.
(b) conformational enantiomers.
(c) configurational diastereomers.
(d) conformational diastereomers.
(e) identical.

18. Which of the following compounds have chiral centers?

I: 1-chloropropane, II: chlorobromomethane, III: 1-chloro-2-methylpropane,
IV: 2-chloro-2-methylbutane.

(a) II, III, IV, (b) I, II, III, (c) II, III, (d) II, (e) III, IV,
(f) None of the previous answers is correct.

19. The compound shown to the right is from the class of compounds known as terpenes. One of the stereoisomers of this structure has been isolated from the plant *Calea prunifolia*. How many stereoisomers of this structure are possible. [Hint: Be careful! Do not blindly apply "rules" without thought. What structural features in this molecule can lead to stereoisomerism? How many of these features are there. Are any meso structures possible. Consequently, how many isomers are possible?]

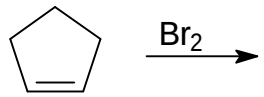


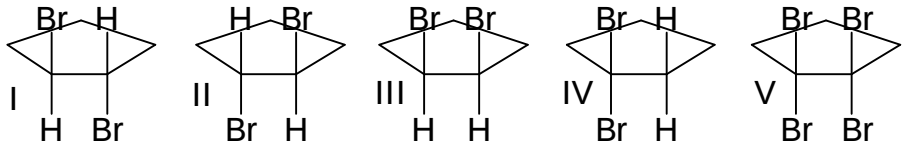
(a) 2, (b) 3, (c) 4, (d) 5, (e) 6, (f) 7, (g) 8

20. Which of the following is not true of enantiomers?

(a) They have the same boiling point. (b) They have the same melting point.
(c) They have the same specific rotation. (d) They have the same density.
(e) They have the same chemical reactivity toward achiral reagents.

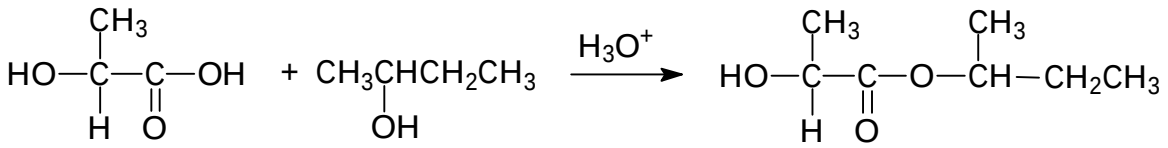
21. Consider the following reaction and select the major product(s).





(a) I, (b) II, (c) III, (d) IV, (e) V, (f) I&II in equal amounts, (g) I&II in unequal amounts, (h) I, II, and III in equal amounts, (i) I, II, and III, with I and II in equal amounts.

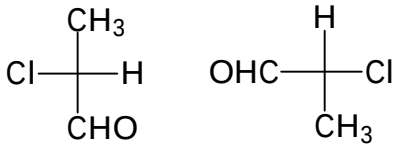
22. Suppose that racemic lactic acid reacts with (S)-2-butanol to form an ester. What is the stereochemical relationship between the two *sec*-butyl lactate esters that form?



lactic acid 2-butanol *sec*-butyl lactate

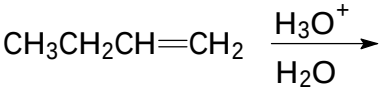
(a) They are enantiomers and would form in equal amount.
(b) They are enantiomers and would form in unequal amount.
(c) They are diastereomers and would form in equal amount.
(d) They are diastereomers and would form in unequal amount.

23. The Fisher projections shown to the right are



(a) enantiomers. (b) diastereomers.
(c) the same molecule.
(d) It is impossible to answer this question from Fisher projections alone.

24. What is (are) the principal product(s) of the following reaction?



(a) $CH_3CH_2CH_2CH_2OH$

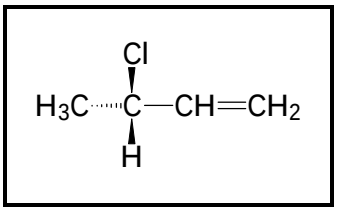
(b) (R-isomer only) $CH_3CH_2CH(OH)CH_3$

(c) (S-isomer only) $CH_3CH_2CH(OH)CH_3$

(d) (unequal amounts of R&S isomers) $CH_3CH_2CH(OH)CH_3$

(e) (equal amounts of R&S isomers) $CH_3CH_2CH(OH)CH_3$

25. (S)-3-chloro-1-butene reacts with HCl by Markovnikov addition. How many Markovnikov products are obtained, counting all stereoisomers?



(S)-3-chloro-1-butene

(a) 1, (b) 2, (c) 3, (d) 4, (e) 5

26. Free radical chlorination of propane produces 1-chloropropane and 2-chloropropane as well as products containing more than one chlorine. If the relative rate of abstraction of hydrogens in this reaction is primary : secondary : tertiary = 1.0 : 3.5 : 5.0, what percentage of the monochloro products is 1-chloropropane?

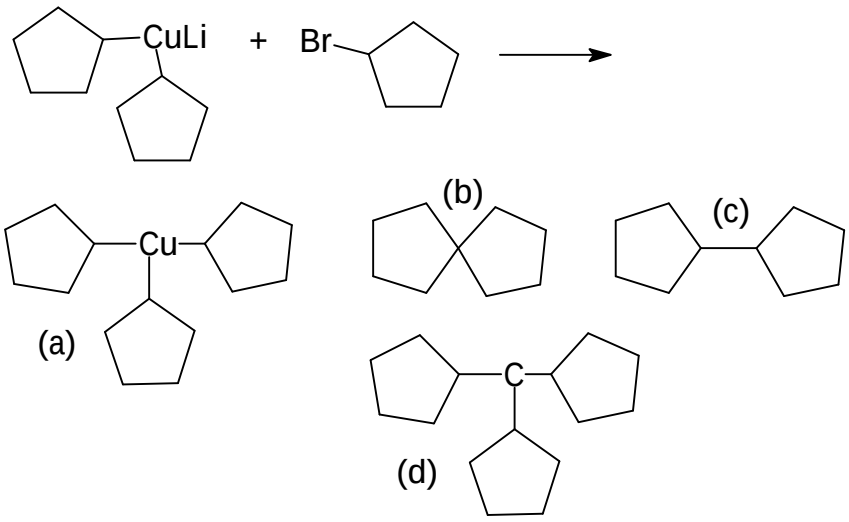
(a) 22%, (b) 29%, (c) 46%, (d) 75%, (e) None of the previous answers is correct.

27. Which of the following alcohols will be most reactive toward HBr in terms of converting the alcohol to an alkyl bromide?

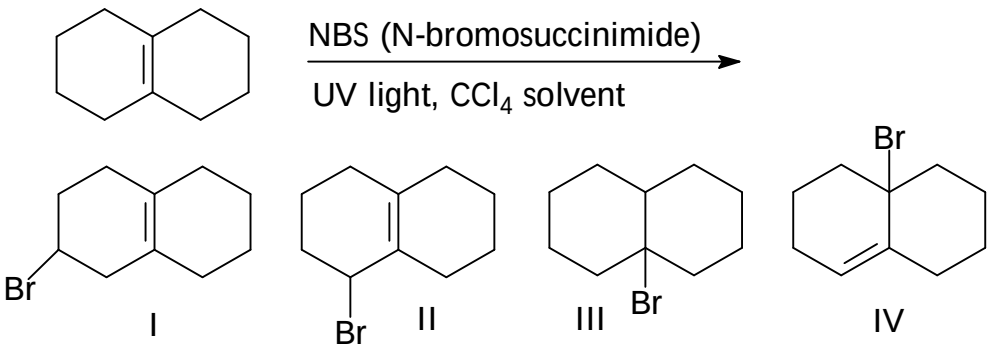
(a) $CH_3CH(OH)CH_2CH_3$ (b) $HOCH_2CH_2CH_2CH_3$ (c) $H_3C-C(CH_3)(OH)-CH_3$

(d) These alcohols would be essentially equally reactive.

28. Select the principal product of the following reaction.



29. Select the two products that form in the following reaction.



(a) I&II, (b) I&III, (c) I&IV, (d) II&III, (e) II&IV, (f) III&IV

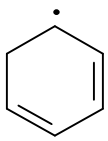
30. Which of the following is not a reactive intermediate in the free radical chlorination of methane?

(a) H•, (b) H_3C•, (c) Cl•, (d) Bogus question. All of them are intermediates.

31. 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

32. How many reasonable resonance structures (including the one shown) can be drawn for the free radical shown to the right.



(a) 2, (b) 3, (c) 4, (d) 5, (e) 6

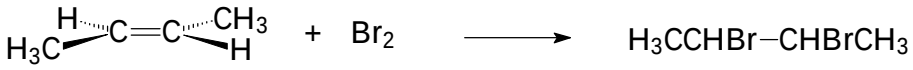
Directions for Part II --- Answer the questions in the space provided. If there is insufficient space continue your answer on the back of the sheet but clearly indicate on the front of the sheet that you have done this.

1. Mechanism. (a) Show the mechanism for the following reaction.

> Be certain to clearly show the configurations around the chiral carbons in the product(s).

> Be certain to show all intermediates and their stereo (3-dimensional) structure(s).

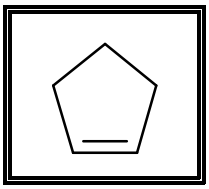
> Be certain to show direction(s) of approach of reacting species if it has stereochemical consequences



(b) Is the product (or product mixture) of this reaction optically active?

(c) Is the product (or products) of this reaction a meso structure, a racemate, or neither?

2. Synthesis. Outline syntheses which would produce each of the following compounds in good yield. You must start each synthesis with cyclopentene, and may use any other materials you need to carry it out. More than one step may be required. [Note: In outlining a synthesis you should show explicitly what compounds you are using and any special conditions. You need not balance equations or show mechanisms; doing so correctly will gain you no additional credit, doing so incorrectly will cost you.]



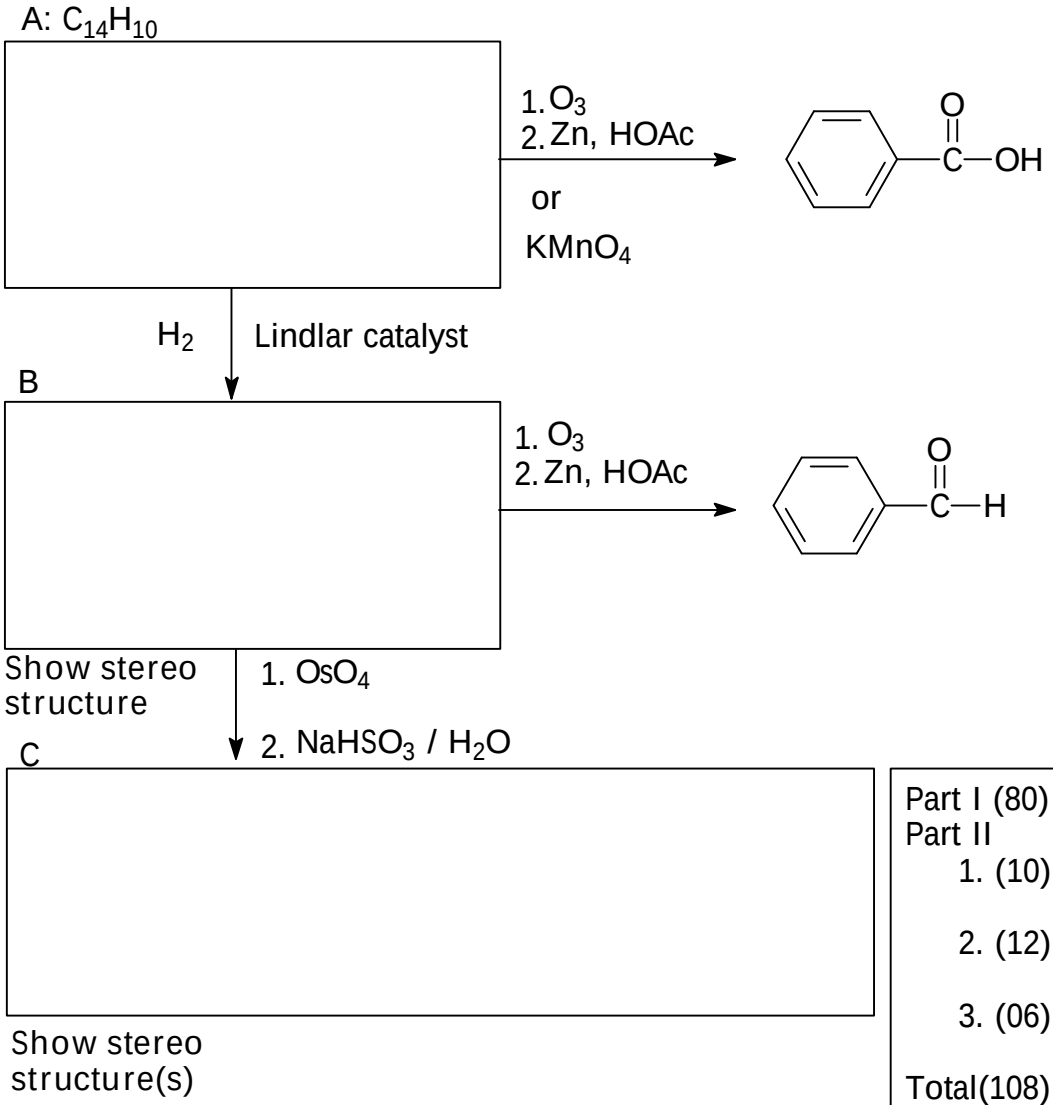
cyclopentene

(a) chlorocyclopentane

(b) methylcyclopentane

(c) 1,3-cyclopentadiene

3. Analysis *aka* a roadmap problem. When compound A, $C_{14}H_{10}$, is treated with ozone or $KMnO_4$, only cyclohexanecarboxylic acid is formed (see below). When compound A is hydrogenated in the presence of Lindar catalyst, compound B is formed. When B is treated with ozone and worked up with zinc and acetic acid, only cyclohexanecarbaldehyde is formed. When B is reacted with osmium tetroxide, OsO_4, and worked up with sodium bisulfite, $NaHSO_3$, in water, compound(s) C is (are) formed [this product may, or may not, consist of more than one stereoisomer]. Show the structures, including stereochemistry, where relevant, of A, B, and C.



Part I (80) _____
Part II
1. (10) _____
2. (12) _____
3. (06) _____
Total(108) _____