

Name \_\_\_\_\_

Department of Chemistry  
SUNY/Oneonta

Chem 221 - Organic Chemistry I

Examination #3 - November 8, 2004

## ANSWERS

### 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 this 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 OSC student (**NOT SOCIAL SECURITY**) number, and the course number (30022101); darken the appropriate bubbles under the entries, making dark black marks which fill the bubbles.

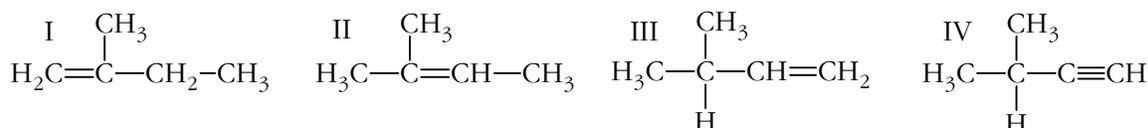
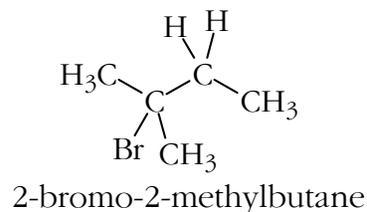
You may use a set of molecular models and the periodic table at the end of the exam, but no other aids, during the exam.

Answer all questions. The questions on Part I are worth 5 points each.

You have 50 minutes. Good luck!

Note: The terms "chiral center" and "stereogenic center" are identical.

1. Treatment of 2-bromo-2-methylbutane with KOH in ethanol yields a mixture of two products. What are they?



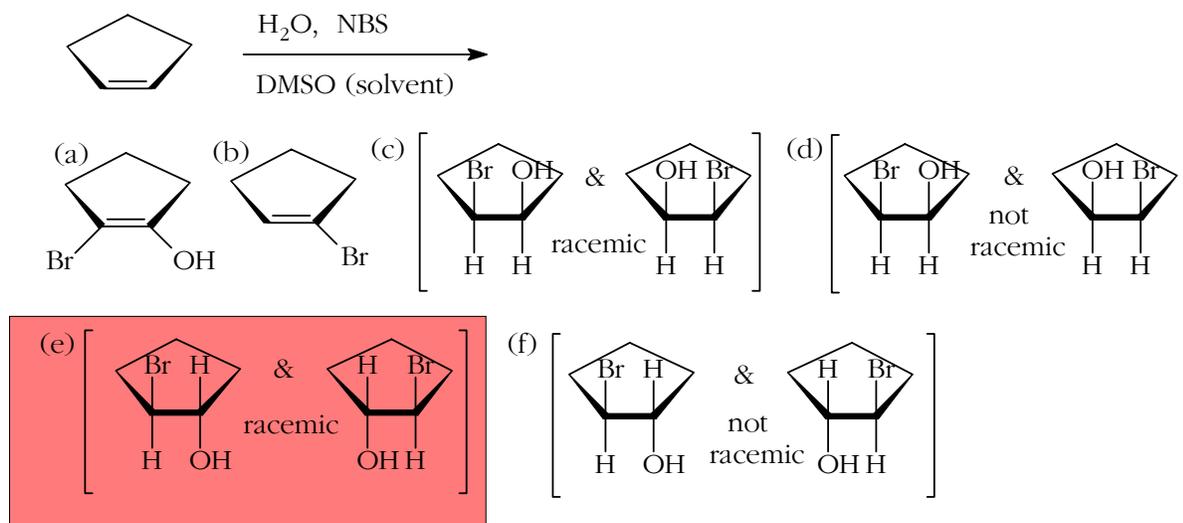
(a) I & II, (b) II & III, (c) III & IV, (d) I & III, (e) II & IV

2. If the reaction in question #1 occurs in one step (no intermediates), which product is likely to be the major product?

(a) I, (b) II, (c) III, (d) IV

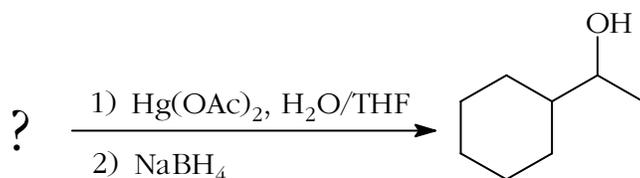
II is more stable than I because it is the more highly substituted alkene. Since the reaction takes place in one step there is only one energy barrier ("hill"). The reaction path leading to the more stable product is likely to involve a smaller barrier in the path; consequently more molecules will follow this path in the reaction.

3. Select the principal product(s) of the following reaction. (NBS = N-bromosuccinimide)

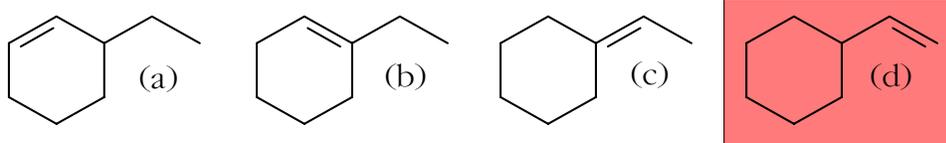


Halohydrin formation involves anti addition, so the OH and Br will be trans to each other. The reactants are achiral so the chiral products must form as a racemic mixture.

4.



Select the alkene which would be the best starting material for the above reaction.

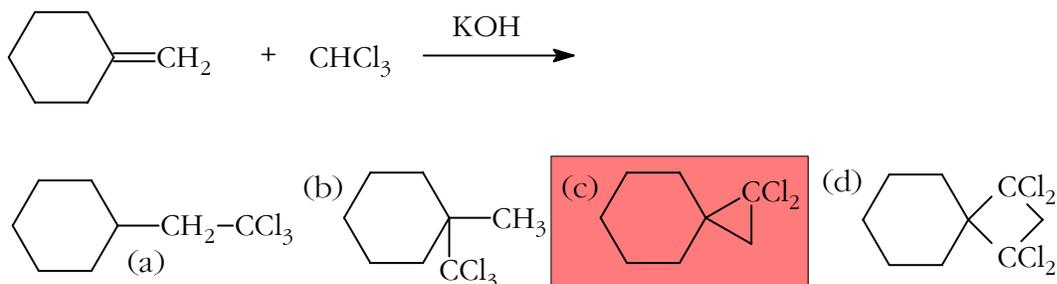


(a) and (b) would not form the product. (c) would form mostly 1-ethyl-1-cyclohexanol (Markovnikov's rule). (d) will form mostly the desired product (Markovnikov's rule).

5. Which procedure would you use to convert 1-pentene to 1-pentanol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ?

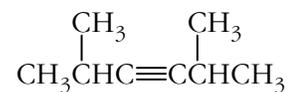
(a) (1)  $\text{Hg}(\text{OAc})_2, \text{H}_2\text{O}/\text{THF}$ ; (2)  $\text{NaBH}_4$ , (b)  $\text{H}_2\text{O}, \text{H}_2\text{SO}_4$ , (c) (1)  $\text{BH}_3$ ; (2)  $\text{KOH}, \text{H}_2\text{O}_2$ ,  
 (d) None of the above answers is correct.  
 (a) & (b) give the Markovnikov alcohol; (c) produces the anti-Markovnikov alcohol.

6. Select the principal product of the following reaction.



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

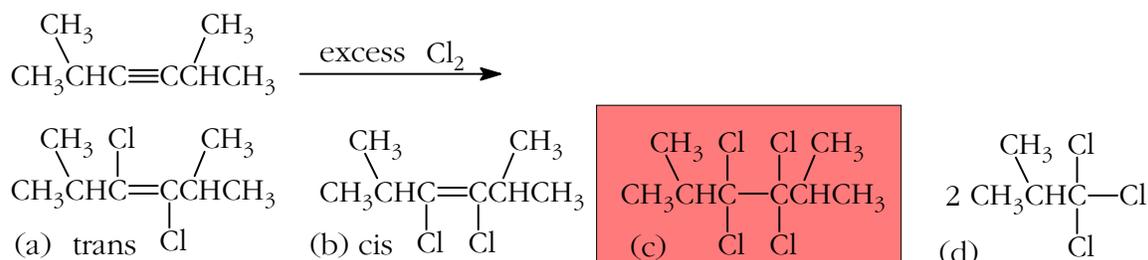
(a) diisopropylacetylene, (b) 2,5-dimethyl-3-hexyne,  
 (c) 2,5-dimethyl-3-hexene, (d) 2-methyl-5-methyl-3-hexyne,  
 (e) None of the previous answers is correct.



8. 1-Butyne can be prepared from 1-butene in two successive synthetic steps. Select the answer which correctly shows these steps.

- (a) 1) HBr; 2) KOH, (b) 1) H<sub>2</sub>/Pt; 2) Br<sub>2</sub>/CCl<sub>4</sub>, (c) 1) Br<sub>2</sub>/CCl<sub>4</sub>; 2) NaNH<sub>2</sub>  
 (d) 1) KOH; 2) HBr

9. Select the principal product of the following reaction.



10. Tautomers are

- (a) constitutional isomers that are in equilibrium with each other.  
 (b) stereoisomers that are in equilibrium with each other.  
 (c) conformational isomers that are in equilibrium with each other.  
 (d) the individual structures we draw when indicating resonance.

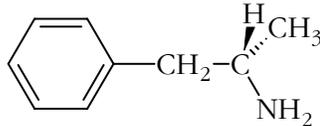
11. In keto-enol tautomerism,

- (a) the keto form is usually favored. (b) the enol form is usually favored.  
 (c) the equilibrium constant is usually about 1.  
 (d) Bogus question! There is no such thing as keto-enol tautomerism.

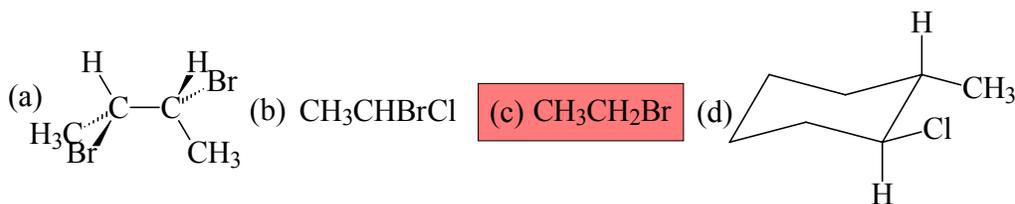
12. To convert 2-butyne to *trans*-2-butene you would use

- (a) lithium in liquid ammonia. (b) hydrogen gas and the Lindlar catalyst.  
 (c) hydrogen gas and a platinum catalyst. (d) a mixture of hydrogen and ammonia gas.

**DIRECTIONS:** Questions 13-14 are of the type where a statement is followed by an explanation: <Statement> **because** <Reason>. For each of these questions select the correct response from those immediately following:

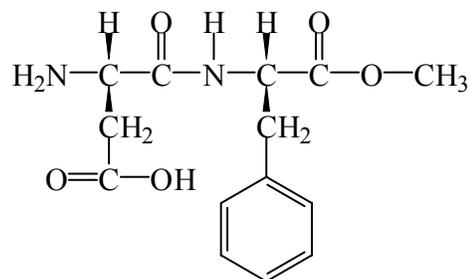
- (a) Both the statement and reason are correct and the reason justifies or explains the statement.  
 (b) Both the statement and reason are correct but the reason does not justify or explain the statement.  
 (c) The statement is false but the reason is true (although it does not apply to the statement).  
 (d) The statement is true but the reason is false.  
 (e) Both the statement and reason are false.
13. The terminal hydrogens on terminal alkynes are more acidic than the vinylic hydrogens of alkenes **because** in the anions that form the unshared pair of electrons is in an  $sp^2$  orbital in the case of the alkenes and in an  $sp^3$  orbital in the case of the alkynes.  
 (d), In the case of alkynes it is an  $sp$  orbital.
14. Alkylation of an acetylide anion using a  $3^\circ$  alkyl halide is not feasible **because** the alkyl halide will undergo elimination rather than substitution.  
 (a)
15. Which of the following objects are chiral: screwdriver, screw, hammer, shoe?  
 (a) screwdriver and screw, (b) hammer and shoe, (c) screwdriver and shoe, (d) screw and hammer, (e) screwdriver and hammer, (e) screw and shoe.  
 (If you selected a different answer you got, ummm, hammered.)
16. Amphetamine (aka benzedrine) is a stimulant that is addictive and was formerly used for weight control. It has one stereogenic center. One of the enantiomers is a stimulant (dexedrine); the other is inactive. The active enantiomer is shown to the right. Which isomer is it?  

- (a) R, (b) S, (c) E, (d) Z

17. Which of the following molecules is **achiral** ?



18. A meso structure is one which  
 (a) has stereogenic centers and is chiral. (b) has stereogenic centers and is achiral.  
 (c) has no stereogenic centers and is chiral. (d) has no stereogenic centers and is achiral.

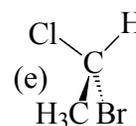
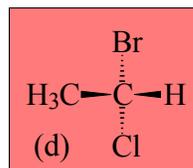
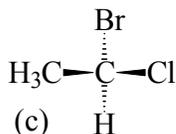
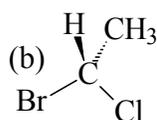
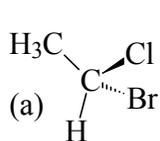
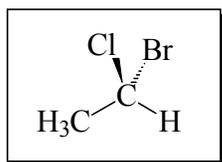
19. The structure of aspartame (G.D. Searle's Nutrasweet®) is shown to the right. How many different stereoisomers are possible for this structure, including the one shown?



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

There are two chiral centers in this molecule;  $n=2$ . Number of stereoisomers due to chiral centers =  $2^n$ , if there are no meso structures. This molecule is very unsymmetrical; it has no plane or center of symmetry – hence no meso structures.

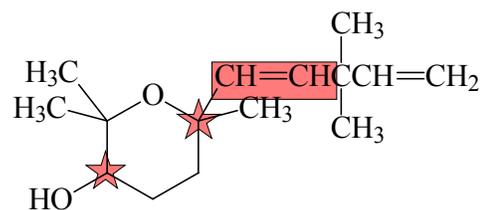
20. Which of the molecules shown below is the enantiomer of the boxed structure?



The boxed structure is R; (d) is S.

\* = a bonus question (5 extra points if you answer it correctly).

- 21\*. 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

The double bond can be E or Z. If it is E, the chiral centers will produce 4 stereoisomers (meso structures not possible here). On the other hand, if it is Z, the same is true; thus, there are 8 stereoisomers in all.

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

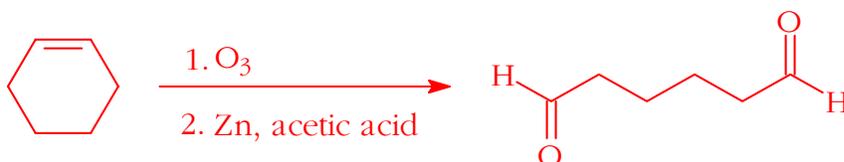
(a) (1)  $\text{H}_2$ , Lindlar catalyst, (2) 1 equivalent  $\text{Br}_2$  in  $\text{CCl}_4$ , (b) (1) 1 equivalent  $\text{Br}_2$  in  $\text{CCl}_4$ , (2)  $\text{BH}_3$ , 3.  $\text{H}_2\text{O}_2$ ,  $\text{KOH}$ , (c) (1)  $\text{Li}$ ,  $\text{NH}_3$ , (2)  $\text{Br}_2$  in  $\text{CCl}_4$ , (d) 2 equivalents  $\text{HBr}$ .

Name \_\_\_\_\_

**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. **Synthesis.** Outline syntheses of the indicated compounds following the constraints imposed in each problem. Show all reagents and important conditions. Do not show mechanisms.

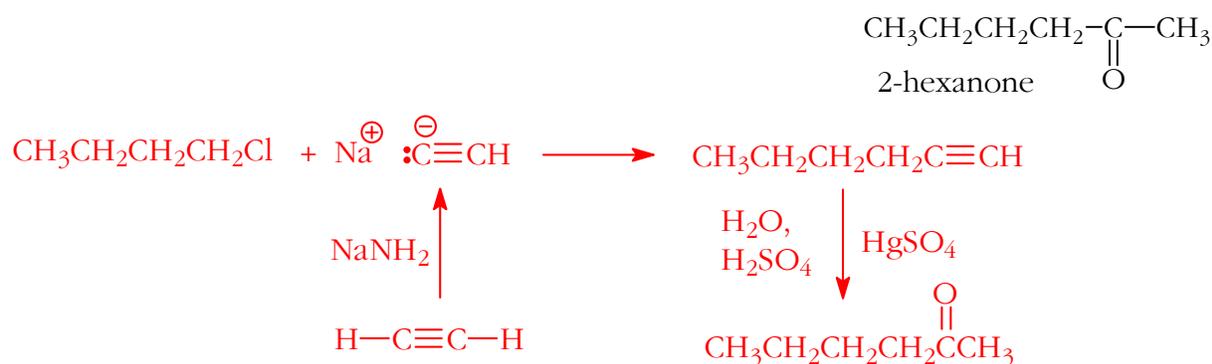
(a) Starting with cyclohexene, and using any other needed materials, make the following compound.



(b) Starting with propyne, and using any other needed materials, make 2,2-dichloropropane.



(c) Make 2-hexanone, starting with organic compounds containing not more than 4 carbons and employing any needed inorganic reagents.



2. **Stereochemistry.** These exercises are of the modified True-False type. If a statement is true, circle the T. If a statement is false, circle the F, *and change the part in italics so that it becomes true.*

- T **F** (a) Optically active molecules that rotate plane-polarized light in a counterclockwise direction are said to be *of S configuration.* **levorotatory**
- T **F** (b) A compound that contains one stereogenic center *may* **must** be chiral; a compound that contains more than one stereogenic center *must* **may** be chiral.
- T** F (c) A *stereogenic center* is an atom in a molecule that is bonded to four different atoms or groups of atoms.
- T **F** (d) *Racemates* Meso molecules are molecules that contain stereogenic centers, but are identical to their mirror images.
- T** F (e) *Diastereomers* are stereoisomers that are not mirror images.
- T **F** (f) Geometric isomers are a type of *enantiomers.* **diastereomers.**
- T** F (g) A reaction mixture that is optically inactive *always* gives a product mixture that is optically inactive.
- T **F** (h) If a molecule does not contain a plane of symmetry it *must* **may** be chiral.
- T** F (i) A 50:50 mixture of two enantiomers is usually separated into its two components by a process known as *resolution.*
- T **F** (j) Cis-1,3-dimethylcyclohexane is *a chiral* **an achiral** compound.

Part I  
100+10(bonus) \_\_\_\_\_

Part II  
1. (15) \_\_\_\_\_

2. (10) \_\_\_\_\_

Total (125+10)\_\_\_\_\_