

Name _____

Department of Chemistry
SUNY/Oneonta

Chem 221 - Organic Chemistry I

Examination #2 - October 19, 1998

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 student (Social Security) number, course number (30022101) and the test number (02); 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 points each.

You have 90 minutes. Good luck!

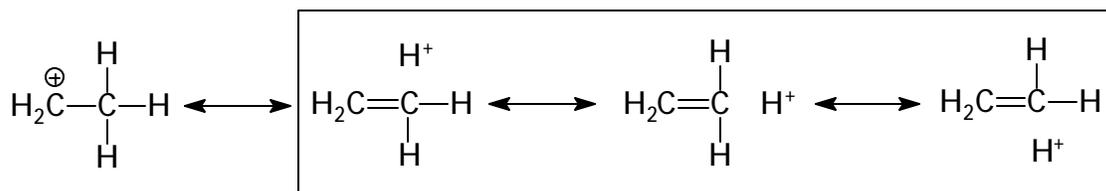
- The reaction of methane with chlorine is an example of
(a) a free radical addition reaction. (b) a polar elimination reaction. (c) a pericyclic substitution reaction. (d) a pericyclic addition reaction. (e) a polar addition reaction. (f) a free radical substitution reaction. (g) a polar substitution reaction.
- The reaction of HBr with 1-butene to give 2-bromobutane as the major product is an example of _____, while, under different conditions, the reaction of HBr with 1-butene to give 1-bromobutane as the major product is an example of _____.
(a) a free radical addition reaction/ a polar elimination reaction. (b) a polar elimination reaction/ a free radical addition reaction. (c) a pericyclic elimination reaction/ a pericyclic addition reaction. (d) a polar addition reaction/ a free radical addition reaction. (e) a free radical addition reaction/ a polar addition reaction.
- The carbon-carbon double bond consists of a σ and a π bond. Which of these bonds is more easily broken (requires less energy to break)?
(a) σ , (b) π , (c) They are equally easy to break. (d) We don't know because both of these bonds are always broken simultaneously.
- Which of the following species would you expect to behave as electrophiles and which as nucleophiles?
Species: (I) H^+ , (II) OH^- , (III) NH_3 , (IV) Mg^{+2}
Answers:
(a) Electrophiles: II, III; Nucleophiles: I, IV
(b) Electrophiles: I, IV; Nucleophiles: II, III
(c) Electrophiles: I, III; Nucleophiles: II, IV
(d) Electrophiles: I; Nucleophiles: II, III, IV
(e) None of the above answers is correct.
- The positively charged carbon in a simple carbocation such as ethyl carbocation, $CH_3CH_2^+$, is
(a) sp^3 hybridized and has a vacant sp^3 orbital.
(b) sp^2 hybridized and has a vacant sp^2 orbital.
(c) sp^3 hybridized and has a vacant p orbital.

(d) sp^2 hybridized and has a vacant p orbital.

DIRECTIONS: Questions 6-8 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.

6. A 3° carbocation is more stable than a 1° carbocation because the charge can be delocalized onto the alkyl groups in the 3° carbocation to a greater extent than is the case for the 1° one, owing to the greater number of alkyl groups in the 3° case.
7. Attempting to demonstrate delocalization of the + charge in a carbocation onto alkyl groups attached to the nominally positively charged carbon by drawing resonance structures of the type shown to the right below is incorrect because if these structures made a contribution the protons would escape owing to their no longer being bonded to the rest of the molecule.



8. A reaction that has a large equilibrium constant as a result of being quite exothermic may or may not have a fast rate of reaction. However, a reaction that has a small equilibrium constant as a result of being quite endothermic must be fairly slow, assuming no unusually large ΔS^\ddagger effects, because ΔH^\ddagger must be at least as large as ΔH° in this case.
9. Which reaction would have the largest K_{eq} , one with $\Delta G^\circ = -50 \text{ kJ/mole}$, one with $\Delta G^\circ = 0$

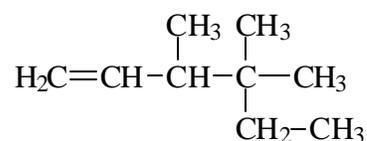
kJ/mole or one with $\Delta G^\circ = +50$ kJ/mole?

- (a) The one with $\Delta G^\circ = -50$ kJ/mole. (b) The one with $\Delta G^\circ = 0$ kJ/mole.
 (c) The one with $\Delta G^\circ = +50$ kJ/mole.
 (d) This question cannot be answered without knowing ΔH° and ΔS° .
 (e) None of the above answers is correct.

10. The $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-$ group is known as

- (a) methylene, (b) vinyl, (c) allyl, (d) benzyl, (e) tosyl

11. Select the IUPAC name for the compound shown to the right.



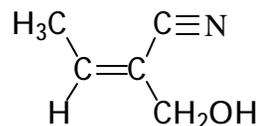
- (a) 3,4,4-trimethyl-1-hexene,
 (b) 4-ethyl-3,4-dimethyl-1-pentene,
 (c) 3,3,4-trimethyl-5-hexene,
 (d) 2-ethyl-2,3-dimethyl-4-pentene,
 (e) None of the above answers is correct.

12. Which of the following compounds can exist as pairs of cis-trans isomers?

- (I) $\text{CH}_3\text{CH}=\text{CH}_2$, (II) $\text{CH}_3\text{CH}=\text{CHCH}_3$, (III) $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$,
 (IV) $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$, (V) $\text{ClCH}=\text{CHCl}$, (VI) $\text{BrCH}=\text{CCl}_2$

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

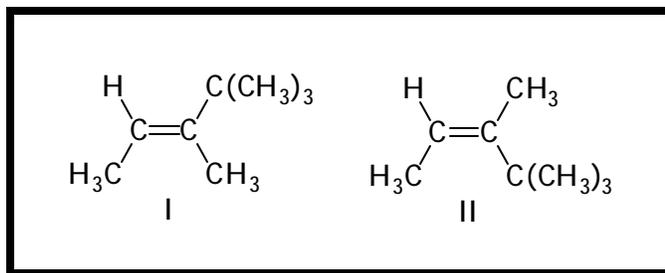
13. Specify the configuration around the double bond in the compound shown to the right using the Cahn-Ingold-Prelog system. [Atomic numbers: H=1, C=6, N=7, O=8]



- (a) A, (b) B, (c) E, (d) X, (e) Y, (f) Z

14. What is the relationship between the two molecules shown to the right?

- (a) There is no relationship.
 (b) They are constitutional isomers.
 (c) They are conformational stereoisomers.
 (d) They are geometric stereoisomers.
 (e) They are stereoisomers, but not of the geometric type.



15. Rank the following alkenes in order of decreasing stability (most stable first).

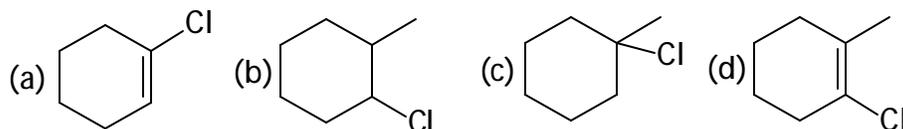
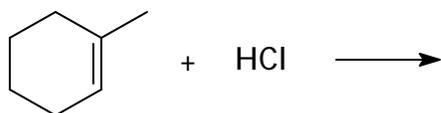
- (I) 1-butene, (II) trans-2-butene, (III) cis-2-butene, (IV) 2-methyl-2-butene,
 (V) 2,3-dimethyl-2-butene

- (a) I>II>III>IV>V, (b) V>IV>III>II>I, (c) V>IV>II>III>I, (d) I>III>II>IV>V,
 (e) Bogus question! All alkenes are deranged.

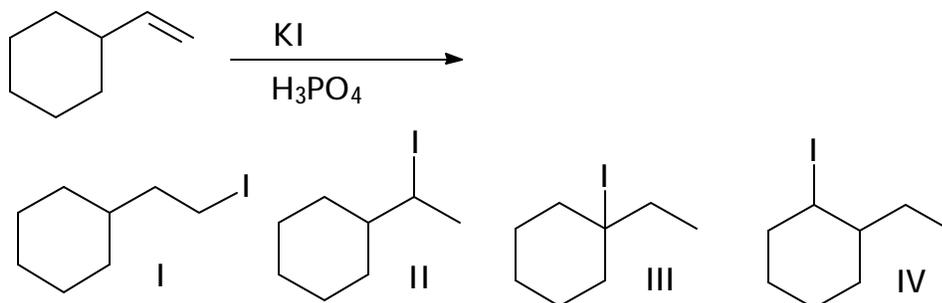
16. Rank the classes (methyl, 1°, 2°, 3°) of carbocation in order of decreasing stability (most stable first).

- (a) methyl > 1° > 2° > 3°, (b) methyl > 1° > 3° > 2°, (c) methyl > 2° > 1° > 3°,
 (d) 3° > 2° > 1° > methyl

17. Select the major product of the following reaction.

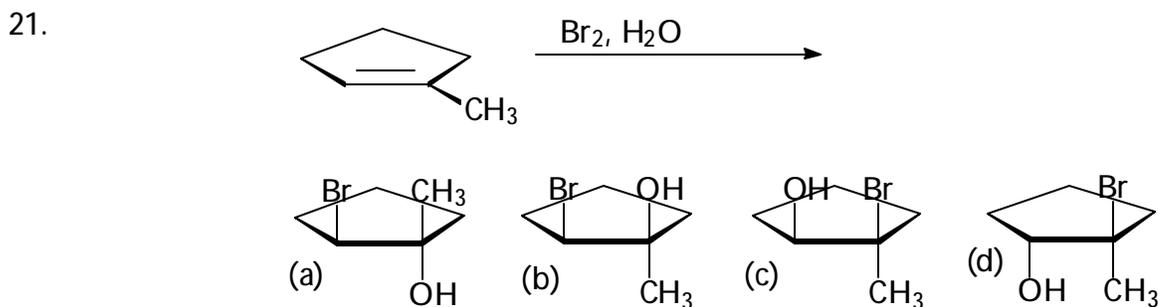


18. Select the answer that best indicates the products that would be formed in significant amounts in the following reaction. [Hint: Think about the mechanism.]

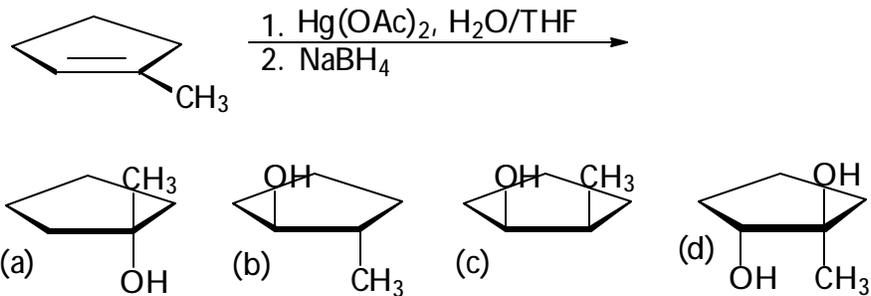


- (a) I&II, (b) II&III, (c) III&IV, (d) I&III, (e) I&IV, (f) II&IV
19. When cyclohexene reacts with bromine in tetrachloromethane 1,2-dibromocyclohexane is formed. This reaction takes place with
- (a) syn stereochemistry. (b) cis stereochemistry. (c) anti stereochemistry.
 (d) random stereochemistry. (e) Stereochemistry is not a feature of this reaction.
20. With regard to question #19, the observed stereochemistry of addition of bromine to cyclohexene is explained by the formation of a _____ intermediate.
- (a) bromonium ion, (b) carbocation, (c) free radical, (d) carbanion,
 (e) Stereochemistry is not a feature of this reaction and this reaction does not involve an intermediate; it takes place in one step.

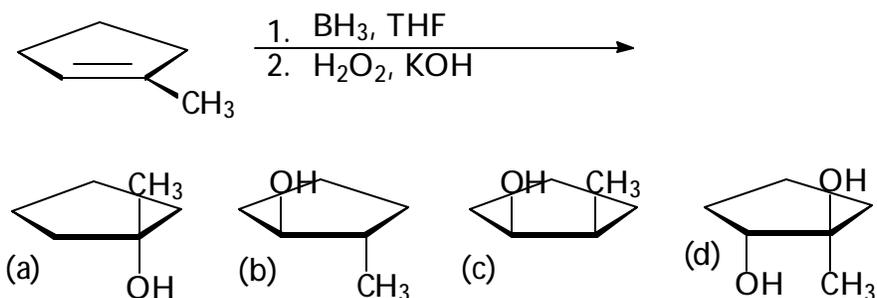
In questions 21 through 26 select the major product of the reaction.



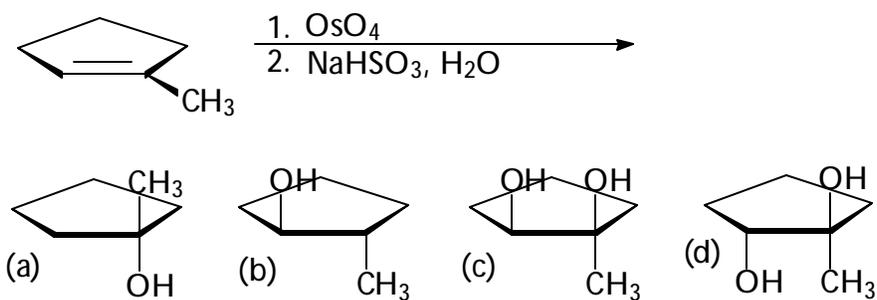
22.



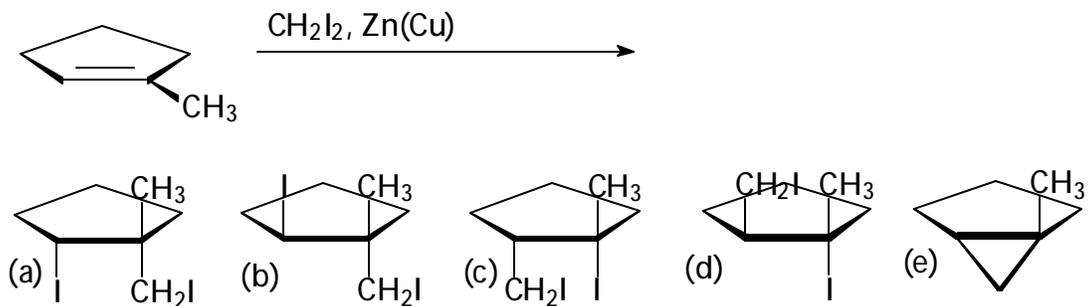
23.



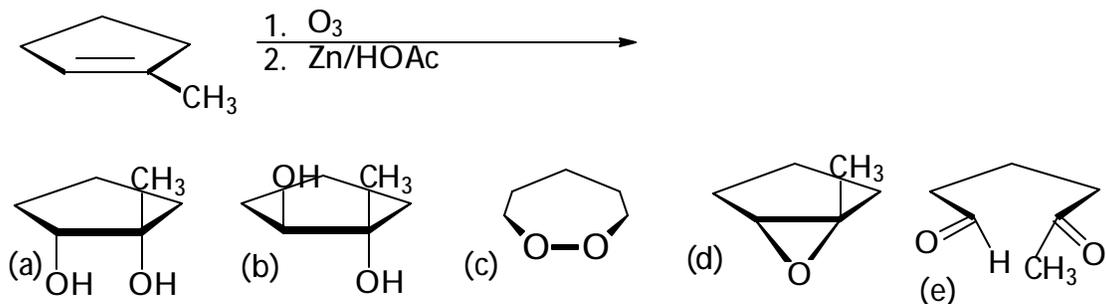
24.



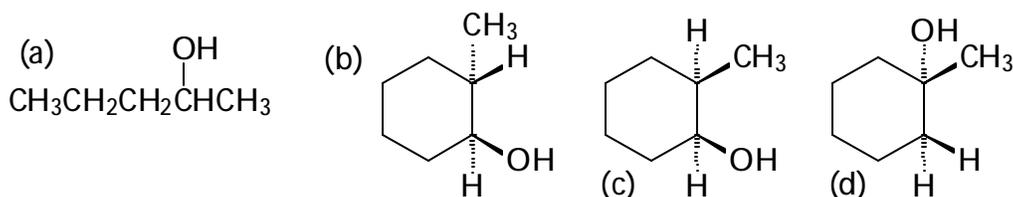
25.



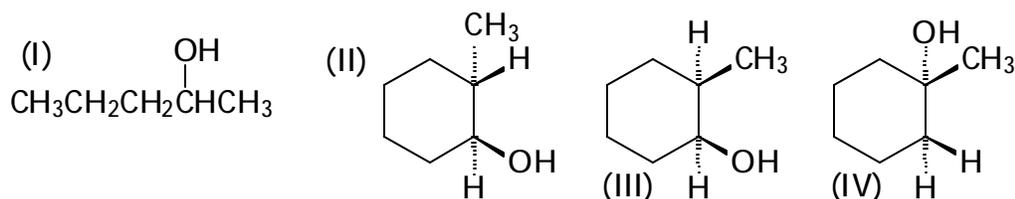
26.



27. Which of the following alcohols could be made selectively by hydroboration/oxidation of an alkene?

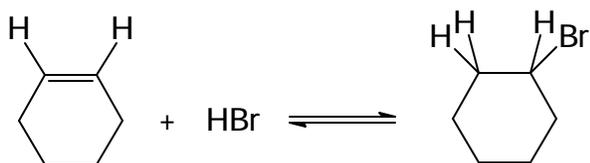


28. Which of the following alcohols could *not* be made selectively by Markovnikov addition of water to an alkene?



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

29. You go into the lab and do an experiment. The experiment consists of adding one mole of HBr to one mole of cyclohexene at room temperature and carefully analyzing the contents of the flask after reaction has stopped. Your analysis reveals that the flask contains 1 mole of bromocyclohexane. You are unable to detect any remaining HBr, cyclohexene, or anything else.



On the basis of your experiment, which of the following conclusions can you draw with great confidence?

I: This is an addition reaction. II: This is an elimination reaction.

III: This is a substitution reaction. IV: This is a polar reaction.

V: This is a free radical reaction. VI: This is a pericyclic reaction.

(a) I, (b) II, (c) III, (d) IV, (e) V, (f) VI, (g) I & IV, (h) I & V, (i) III & IV,

(j) None of the above answers is correct.

30. Based on your results (question #29), it would appear that the equilibrium constant for the reaction of HBr with cyclohexene to give 1-bromocyclohexane is quite large at room temperature (you do not detect any left over reactants). If you carried out the reaction at a substantially higher temperature, would you expect the equilibrium constant to be larger, unchanged, or smaller?

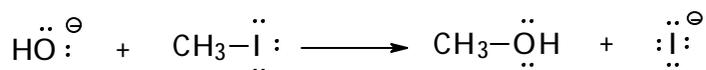
[Hint: It may help to consider the equation, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, in a semi-quantative way, in working out the answer to this question. This question is not unrelated to the situation which exists in the dimerization-of-cyclopentadiene/cracking-of-dicyclopentadiene reaction.]

(a) smaller, (b) larger, (c) unchanged

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. Later this semester you will investigate the rate of the following reaction by dissolving iodomethane and potassium hydroxide in a mixture of water and ethanol and tracking the decrease in concentration of hydroxide ion with time.
- (a) Using the relevant bond dissociation energies provided, calculate an approximate ΔH° for this reaction. If you want credit for your answer, *clearly* show your work.

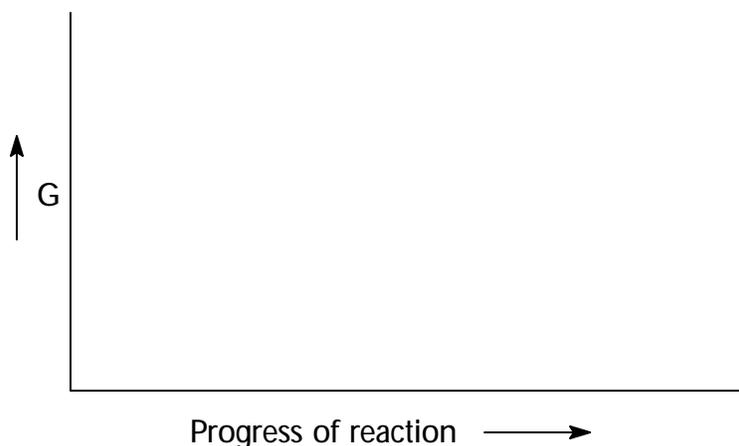


<u>Bond</u>	<u>D (kJ/mol)</u>	<u>Bond</u>	<u>D (kJ/mol)</u>
CH ₃ -I	234	(CH ₃) ₃ C-I	209
H-I	298	(CH ₃) ₃ C-H	390
CH ₃ -H	438	(CH ₃) ₃ C-OH	381
CH ₃ -OH	380		

Based on your calculation, is the reaction *exothermic* or *endothermic*?

- (b) Explain one reason why the value you calculated above is only an approximate value for ΔH° .

(c) Sketch a reaction coordinate diagram for this reaction and label reactants, products, transition state, ΔG° , and ΔG^\ddagger .

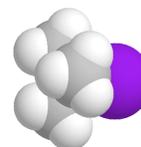


(d) Iodoethane, $\text{CH}_3\text{CH}_2\text{-I}$, reacts with hydroxide ion by the same mechanism as iodomethane (to give $\text{CH}_3\text{CH}_2\text{-OH}$), but more slowly. 2-Iodopropane reacts by this mechanism still more slowly and 2-iodo-2-methylpropane, $(\text{CH}_3)_3\text{C-I}$, reacts so slowly that we would say that it does not react by this mechanism.

(i) Clearly describe the details of the mechanism for the reaction between iodomethane and hydroxide ion.



Iodomethane

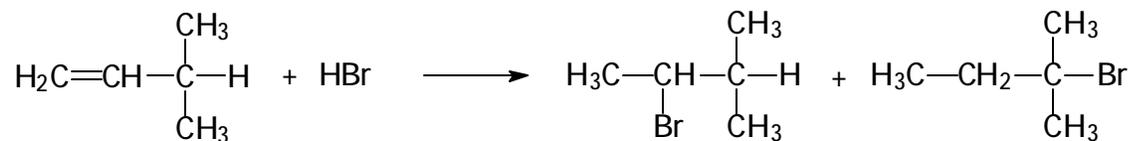


2-Iodo-2-methylpropane

(ii) Clearly describe why 2-iodo-2-methylpropane reacts so slowly by this mechanism. In your description be sure to indicate which of the rate determining factors (collision frequency factor, energy factor, probability factor) is/are involved in an important way.

[Hint: The use of molecular models may be helpful here.]

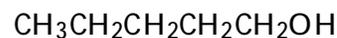
2. (a) Clearly show all steps in the mechanism of the following reaction. Show the structures of all intermediates, but not transition states. Be sure to clearly show how each product is formed.



- (b) Explain why $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_2\text{C}-\text{CH}_2-\text{C}-\text{H} \\ | \\ \text{Br} \quad \text{CH}_3 \end{array}$ is hardly formed in this reaction.

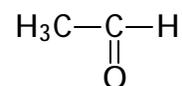
3. Synthesis. Outline syntheses which would produce each of the following compounds in good yield. You must start your synthesis with the indicated starting material, and may use any other materials you need to carry it out. More than one step may be required. [Note: In outlining a synthesis you should 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.]

(a) Synthesize 1-pentanol, from a hydrocarbon containing not more than 5 carbons.



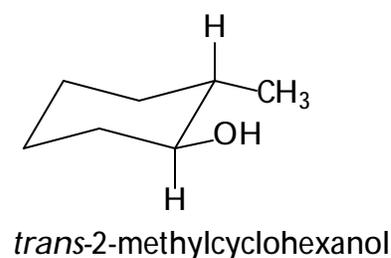
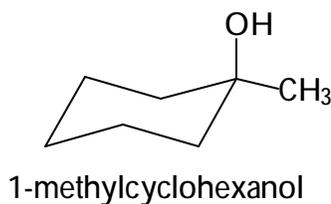
1-pentanol

(b) Synthesize the compound shown to the right starting with an alkene of your choice.



acetaldehyde

(c) Synthesize *trans*-2-methylcyclohexanol from 1-methylcyclohexanol.



Part I (60)	_____
Part II	_____
1.(15)	_____
2.(10)	_____
3.(15)	_____
Total(100)	_____