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 (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 2.5 points each.

You have 90 minutes. Good luck!
Questions 1-5 consist of pairs of structures. Select the best description of each pair from the list which follows the structures. [You may or may not have to use a description more than once to correctly answer all of these questions.]

(a) conformational stereoisomers, (b) conformational constitutional isomers, (c) stereoisomers but not cis-trans isomers, (d) cis-trans stereoisomers, (e) constitutional isomers, (f) not isomers

6. Which of the conformers of butane shown has the highest energy?

(a) anti-periplanar (b) anti-clinal (c) syn-periplanar (d) syn-clinal

7. Consider cis-1-\(\tau\)-butyl-4-methylcyclohexane. The preferred chair conformation for this molecule will have

(a) \(\tau\)-butyl axial and methyl axial. (b) \(\tau\)-butyl equitorial and methyl equitorial.
8. The chair conformation of cyclohexane is strain free. The boat conformation of cyclohexane

(a) is also strain free. (b) has torsional strain, only. (c) has steric strain, only.
(d) has angle strain, only. (e) has torsional and angle strain.
(f) has torsional and steric strain. (g) has angle and steric strain.
(h) has torsional, angle, and steric strain.

9. 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.

10. Given the bond dissociation energies below, what would you expect the approximate $\Delta H^\circ$ for this reaction to be (in kcal/mole)?


(a) +15, (b) -15, (c) +311, (d) -311, (e) 0

11. Based on your results, 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-cyclopentadiene/cracking-of-dicyclopentadiene reaction.]

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

12. Which of the following species would you expect to behave as electrophiles and which as nucleophiles?

\[ \text{Species: } (I) \ H^+, \quad (\overline{II}) \ \text{H}-\text{OH}_2\text{C}^+ \text{C}^\equiv \text{C}_2\text{H}_2, \quad (IV) \ \text{BF}_3 \quad (V) \ \text{H}_2\text{C}^=\text{CH}_2 \]

**Answers:**
(a) Electrophiles: II, III, V; Nucleophiles: I, IV
(b) Electrophiles: I, IV; Nucleophiles: II, III, V
(c) Electrophiles: I, III, IV; Nucleophiles: II, V
(d) Electrophiles: I; Nucleophiles: II, III, IV, V
(e) None of the above answers is correct.

13. Despite the limitations of radical chlorination of hydrocarbons, the reaction is still useful for synthesizing certain chlorinated compounds. For which of the following compounds does radical chlorination give single monochlorinated products (i.e., does not give a mixture of constitutionally isomeric monochlorinated products)?

**Compounds:**
(\text{I}) \ \text{C}_2\text{H}_6 \quad (\text{II}) \ \text{CH}_3\text{CH}_2\text{CH}_3 \quad (\text{III}) \ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \quad (\text{IV}) \ \text{CH}_3\text{CCH}_2\text{CH}_3 \quad (V) \ \text{CH}_3 \quad (VI) \ \text{C}_6\text{H}_{12}

**Answers:**
(a) I & II, (b) III & IV,
(c) V & VI, (d) I, III, V, (e) II, IV, VI, (f) I, III, VI, (g) III, V, VI

14. Vitamin A has the molecular formula \text{C}_{20}\text{H}_{30}\text{O}. How many degrees of unsaturation does vitamin A have?

(a) 2, (b) 3, (c) 4, (d) 5, (e) 6, (f) 7, (g) None of these answers is correct.

15. When vitamin A is exhaustively hydrogenated with excess hydrogen over a platinum catalyst a compound of molecular formula \text{C}_{20}\text{H}_{30}\text{O} results. How many rings does vitamin A contain?

(a) 0, (b) 1, (c) 2, (d) 3, (e) None of these answers is correct.
16. The IUPAC name of the compound shown to the right is
   (a) 2-ethyl-1-pentene,  (b) 4-ethyl-4-pentene,
   (c) 3-methylenexane,  (d) 1-ethyl-1-propylethene
   (e) None of these answers is correct.

17. The name of the compound shown to the right is
   (a) 1-isopropyl-3-methyl-5-cyclohexene,
   (b) 3-isopropyl-1-methyl-5-cyclohexene,
   (c) 3-isopropyl-5-methylcyclohexene,
   (d) 2-isopropyl-4-methylcyclohexene,
   (e) 6-isopropyl-4-methylcyclohexene,
   (f) 5-isopropyl-3-methylcyclohexene

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

   **Compounds:**
   
   ![Chemical structures]

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

19. Determine whether the following compound is the E or Z isomer.
    [Atomic numbers: H=1, C=6, F=9]
   (a) E,  (b) Z,  (c) Q,  (d) r,  (e) U

20. The initiation step in free radical chlorination of alkanes involves
    the following reaction.
    
    ![Chemical structure]
    This reaction can be characterized as
    (a) homolytic.  (b) heterolytic.
    (c) homogenic.  (d) heterogenic.

21. *Cis*-2-butene and *trans*-2-butene are known as *cis-trans* or geometric isomers. These isomers are
(I) structural, (II) stereoisomers, (III) configurational, (IV) conformational

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

22. Arrange the following compounds in order of decreasing stability (most stable first).

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

23. When HCl adds to propene the addition is regioselective: 2-chloropropane is the major product; little 1-chloropropane is formed. Part of the explanation for this regioselectivity has to do with more stable carbocations being formed faster than less stable ones. Theoretical support for the idea that more stable carbocations would be formed faster than less stable ones comes, in part, from

(a) the Hammond postulate. (b) Markovnikov's rule. (c) Sadtzef's rule.
(d) the Diels-Alder rule. (e) the golden rule.

24. Rank the following carbocations in order of decreasing stability (most stable first).

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

25. Shown below are three postulated mechanisms for the addition of bromine to cyclopentene. In each case the product would be 1,2-dibromocyclopentane. However, the stereochemistry of the product could be affected by the mechanism. In other words, one mechanism might give the E- isomer, another the Z- isomer, and another a mixture of E- and Z- isomers. You are to select the answer which correctly indicates the stereochemical outcome for each postulated mechanism.
Mechanism I

\[ \text{Br} \quad \text{Br} \quad \rightarrow \quad 1,2\text{-dibromocyclopentane} \]

Mechanism II

\[ \text{Br} \quad \text{Br} \quad + \quad \text{Br}_2 \quad \rightarrow \quad \text{H} \quad \text{Br} \quad + \quad \text{Br} \quad \rightarrow \quad 1,2\text{-dibromocyclopen} \]

Mechanism III

\[ \text{Br} \quad \text{Br} \quad + \quad \text{Br}_2 \quad \rightarrow \quad \text{H} \quad \text{H} \quad + \quad \text{Br} \quad \rightarrow \quad 1,2\text{-dibromocycloper} \]
<table>
<thead>
<tr>
<th>ANSWERS</th>
<th>Mechanism I</th>
<th>Mechanism II</th>
<th>Mechanism III</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ---&gt;</td>
<td>E</td>
<td>E &amp; Z</td>
<td>Z</td>
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<tr>
<td>(b) ---&gt;</td>
<td>Z</td>
<td>E</td>
<td>E</td>
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<tr>
<td>(c) ---&gt;</td>
<td>Z</td>
<td>E &amp; Z</td>
<td>E</td>
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<tr>
<td>(d) ---&gt;</td>
<td>Z</td>
<td>E &amp; Z</td>
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26. Which of the mechanisms in question #25 could have a reaction coordinate diagram similar to the one shown here.

(a) I, (b) II, (c) III, (d) I&II, (e) II&III
(f) I&III, (g) I-III
(h) None of the mechanisms could have a reaction coordinate similar to the one here.

27. It has been found that ionization of 3-bromo-2-fluoro-2-methylbutane in SbF₅/liquid SO₂ leads not to an open carbocation, but, rather, to a bromonium ion.

\[
\text{(CH}_3\text{)_2C} - \text{CH CH}_3 \xrightarrow{\text{liquid SO}_2} \text{SbF}_5^+ \quad \text{H}_3\text{C} - \text{C} - \text{CH}_3
\]

[This work was done by George Olah who recently won the 1994 Nobel Prize in Chemistry.]

Which of the following is the most reasonable assessment of the contribution this discovery makes to determining the reaction mechanism for the bromination of alkenes (see question #25):

(a) This discovery leaves no doubt that Mechanism III is correct.
(b) This discovery leaves no doubt that Mechanism II is correct.
(c) This discovery provides some indirect support for mechanism III by showing that bromonium ions are formed in preference to open carbocations (Mechanism II), at least under the conditions employed here, which, it must be admitted, are different from the usual conditions for bromination of alkenes.
(d) This discovery leaves no doubt that Mechanism II is incorrect.

28. Which product(s) are formed in substantial amount in the following reaction.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{H}
\end{align*}
\]

\[+ \quad \text{HCl} \quad \rightarrow \quad ?\]

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

29. An unknown unsaturated compound is subjected to the ozonolysis-zinc reduction sequence and the only product is the compound shown to the right. Which of the following compounds could the unknown be?

(a) \(\text{(a)}\) \quad (b) \(\text{(b)}\) \quad (c) \(\text{(c)}\) \quad (d) \(\text{(d)}\)

30. The positive charge residing on the positively charged carbon in an alkyl carbocation is the result of a vacant _____ orbital.

(a) sp\(^3\), (b) sp\(^2\), (c) sp, (d) s, (e) p, (f) \(\sigma\), (g) \(\pi\)
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. Draw the structure of the major organic product of the reaction of 1-methylcyclopentene with each of the following sets of reagents.

(a) $\text{BH}_3 \xrightarrow{1. \text{H}_2\text{O}_2, \text{KOH}} \text{H}_2\text{O}_2 \xrightarrow{2. \text{NaBH}_4} \text{[Show which stereoisomer(s) (i.e., formed by doing (a) 3-D drawing]}

(b) $\text{Hg(OAc)}_2, \text{H}_2\text{O} \xrightarrow{1. \text{NaBH}_4} \text{[Show which stereoisomer(s) (i.e., formed by doing (a) 3-D drawing]}

(c) $\text{CH}_2\text{I}_2 \xrightarrow{\text{Zn(Cu), ether}} \text{[Show which stereoisomer(s) (i.e., formed by doing (a) 3-D drawing]}

(d) $\text{HBr peroxide} \xrightarrow{\text{peroxide}} $
2. 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 2-pentanol, from a hydrocarbon containing not more than 5 carbons.

(b) Synthesize the compound shown to the right from cyclopentene.

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

Part I (75) _______
Part II---
  1. (16) _______
  2. (9) _______
Total (100)________