Solutions

Department of Chemistry
SUNY/Oneonta

Chem 221 - Organic Chemistry I

Examination #2 - October 23, 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 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.

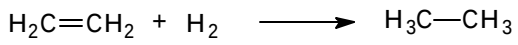
Answer all questions. The questions on Part I are worth 2.5 points each.

You have 90 minutes. Good luck!

1. 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.

2. The reaction shown below can be classified as a(n) _____ reaction.



(a) addition, (b) elimination, (c) substitution, (d) rearrangement

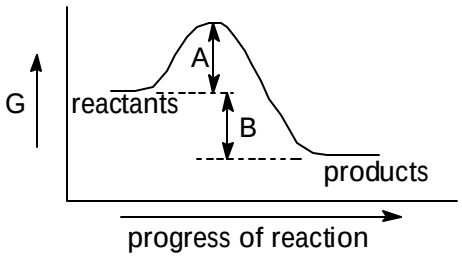
3. At 25° C. the value of ΔG^o for a reaction is -50 kJ/mole. Select the answer that correctly indicates what we know about this reaction.

Answer	K_{eq}	ΔS^o	Rate
(a)	> 1	> 1	fast
(b)	< 1	unknown	slow
(c)	unknown	< 1	fast
(d)	> 1	unknown	unknown
(e)	< 1	< 1	unknown

4. In a reaction energy diagram, an energy maximum would indicate a

(a) reactant. (b) product. (c) intermediate. (d) transition state. (e) Any of the above (a-d) could be the maximum in such a diagram. (f) reactant or product, depending on the reaction.

Consider the reaction energy diagram to the right in answering questions 5 and 6.



5. The quantity "A" in the above diagram represents _____ for the reaction.

(a) $\Delta G^{\ddagger}$, (b) ΔG^{o}, (c) $\Delta H^{\ddagger}$, (d) ΔH^{o}, (e) None of the previous answers is correct.

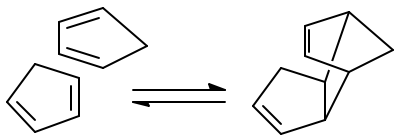
6. This reaction is

(a) exergonic. (b) endergonic. (c) excretory. (d) endcretory.

7. Which of the following is likely to be a nucleophile and which an electrophile?
Note: These are Lewis structures, but formal charges are not shown. Two of the species are ions and in these cases the net ionic charges are shown.

Answer	$H_3O:^{+1}$	BF_3	$:C{\equiv}N:^{-1}$
(a)	electrophile	electrophile	electrophile
(b)	nucleophile	nucleophile	nucleophile
(c)	electrophile	nucleophile	nucleophile
(d)	electrophile	electrophile	nucleophile
(e)	electrophile	nucleophile	electrophile

8. Consider the reaction equilibrium shown to the right. Two cyclopentadiene molecules join together to form one dicyclopentadiene. In this process two π bonds are broken and two σ bonds form.



cyclopentadiene dicyclopentadiene

If one were to increase the temperature of the cyclopentadiene/dicyclopentadiene mixture, the equilibrium would likely

(a) shift to the right (i.e. more dicyclopentadiene would form from cyclopentadiene). (b) shift to the left. (c) remain unchanged. (d) change in such a way that more cyclopentadiene and more dicyclopentadiene would be produced. (e) change in such a way that the amounts of both cyclopentadiene and dicyclopentadiene would decrease.

9. Consider an overall reaction that mechanistically consists of two sequential steps. Under a certain set of conditions the second step is twice as fast as the first step. Under these conditions the final product will be formed

(a) at the same rate as the first step. (b) at the same rate as the second step. (c) at a rate half way between that of the first and second steps. (d) at a rate that is the rate for the first step multiplied by the rate for the second step. (e) at a rate that is the sum of the rates for the first and second steps.

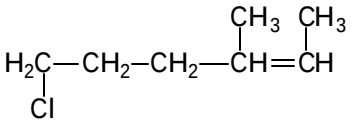
10. Which of the following statements is true?

(a) A nucleophile is a Lewis acid and an electrophile is a Lewis base.
(b) A nucleophile is a Lewis base and an electrophile is a Lewis acid.
(c) A nucleophile is a Bronsted-Lowry acid and an electrophile is a B-L base.
(d) A nucleophile is a Bronsted-Lowry base and an electrophile is a B-L acid.

11. Calculate the degree of unsaturation for compounds that have the molecular formula C_8H_{14}.

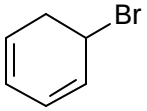
(a) 1, (b) 2, (c) 3, (d) 4, (e) None of the previous answers is correct.

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



(a) 5-chloro-1,2-dimethyl-1-pentene,
(b) 6-chloro-3-methyl-2-hexene, (c) 1-chloro-4,5-dimethyl-4-pentene,
(d) 1-chloro-4-methyl-4-hexene

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



(a) 5-bromo-1,3-cyclohexadiene, (b) 6-bromo-1,3-cyclohexadiene,
(c) 1-bromo-2,4-cyclohexadiene, (d) 1-bromo-3,5-cyclohexadiene,
(e) 1-bromo-2,4-cyclohexene

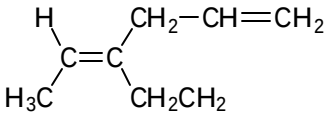
14. *Cis*- and *trans*-2-butene are

(a) conformational stereoisomers. (b) configurational stereoisomers.
(c) constitutional isomers. (d) not isomers.

15. The double bond in an alkene

(a) consists of a σ-bond and a π-bond and the π-bond is stronger than the σ-bond.
(b) consists of a σ-bond and a π-bond and the σ-bond is stronger than the π-bond.
(c) consists of a σ-bond and a σ*-bond and the σ-bond is stronger than the σ*-bond.
(d) consists of a π-bond and a π*-bond and the π-bond is stronger than the π*-bond.

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



(a) (E)-3-ethyl-2,5-hexadiene, (b) (Z)-3-ethyl-2,5-hexadiene,
(c) (E)-4-ethyl-1,4-hexadiene, (d) (Z)-4-ethyl-1,4-hexadiene

17. The necessary and sufficient condition for an alkene to exhibit geometric (cis/trans) isomerism is that

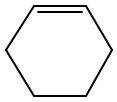
(a) all four groups attached to the carbons joined by the double bond must be different.
(b) both groups attached to one of the carbons joined by the double bond must be the same.
(c) both groups attached to one of the carbons joined by the double bond must be different from each other.
(d) both groups attached to one of the carbons joined by the double bond must be different from each other and both groups attached to the other carbon joined by the double must be different from each other.

18. With regard to *cis*- and *trans*-2-butene it is true that

(a) *trans*-2-butene is more stable because of steric strain in *cis*-2-butene.
(b) *trans*-2-butene is less stable because of steric strain in *trans*-2-butene.
(c) *trans*-2-butene is more stable because of torsional strain in *cis*-2-butene.
(d) *trans*-2-butene is less stable because of torsional strain in *trans*-2-butene.

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

Compounds:

I 

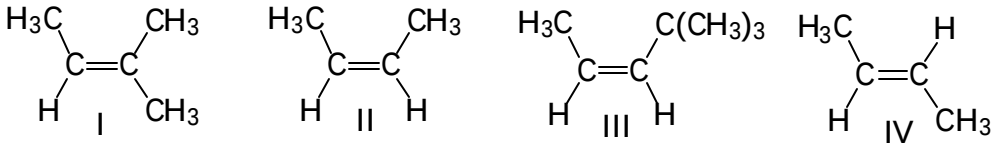
$CH_3CH{=}CH_2$ II

$(CH_3)_2C{=}CHCH_3$ III

$ClCH{=}CHCl$ IV

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

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



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

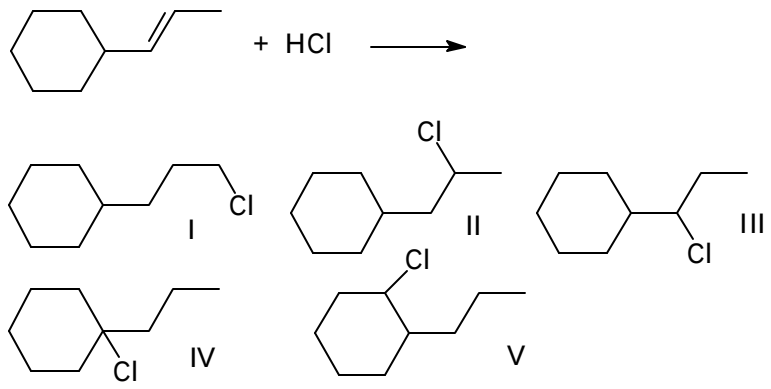
21. Markovnikov's Rule: In the addition of HX to an alkene, the H attaches to the doubly bonded carbon with the _____ alkyl groups and the X attaches to the doubly bonded carbon with the _____ alkyl groups.

<u>(a) smaller number of / greater number of</u>, (b) greater number of / smaller number of,
(c) smaller / larger, (d) larger / smaller

22. 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

<u>(a) the Hammond postulate</u>. (b) Markovnikov's rule. (c) Saytzeff's rule.
(d) the Diels-Alder rule. (e) the golden rule.

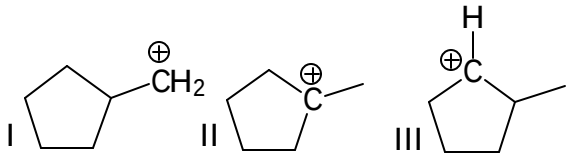
23. Which of the products shown would actually form in the following reaction?



(a) I&IV, (b) I&V, (c) II&III, <u>(d) II-IV</u>, (e) III-V

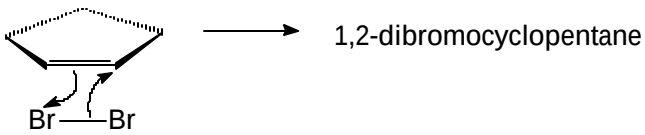
24. Rank the following carbocations in order of decreasing stability (most stable first).

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

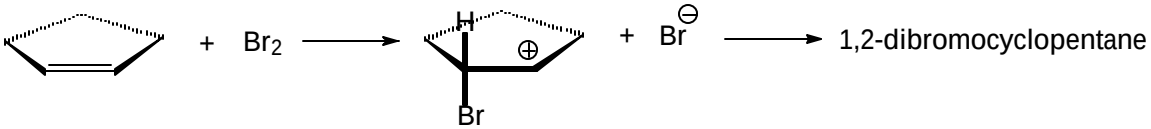


25. Shown below are three postulated mechanisms for the addition of bromine to cyclopentene. In each case the product would be 1,2-dibromocyclopentane. However, the stereochemistry of the product could be affected by the mechanism. In other words, one mechanism might give the *cis* isomer, another the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

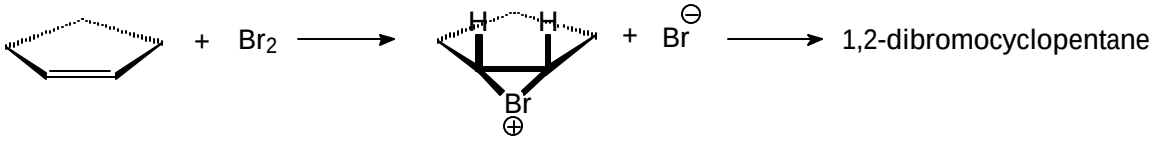
Mechanism I



Mechanism II



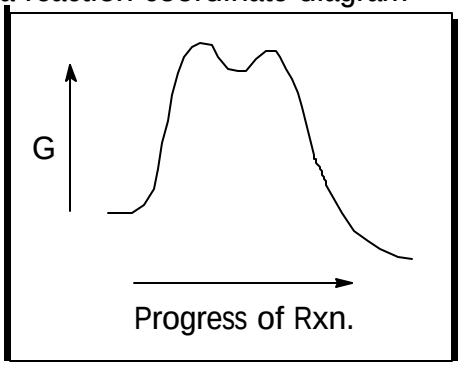
Mechanism III



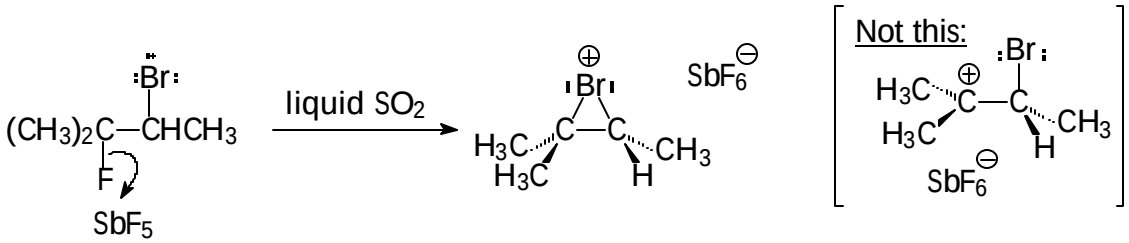
ANSWERS	Mechanism I	Mechanism II	Mechanism III
(a) --->	trans	trans & cis	cis
(b) --->	cis	trans	trans
(c) --->	cis	trans & cis	trans
(d) --->	cis	trans & cis	trans & cis

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 SbF_5/liquid SO_2 leads not to an open carbocation, but, rather, to a bromonium ion.



[This work was done by George Olah who 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.

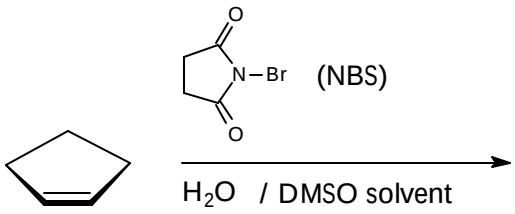
(b) This discovery leaves no doubt that Mechanism II is correct.

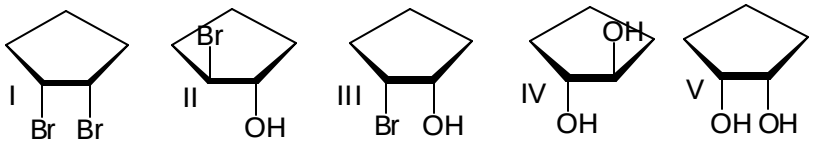
(c) This discovery provides some indirect support for mechanism III by showing that bromonium ions are formed in preference to open carbocations (Mechanism II), at least under the conditions employed here, which, it must be admitted, are different from the usual conditions for bromination of alkenes.

(d) This discovery leaves no doubt that Mechanism II is incorrect.

In questions 28-30 select the answer that correctly lists the products that are formed, as indicated.

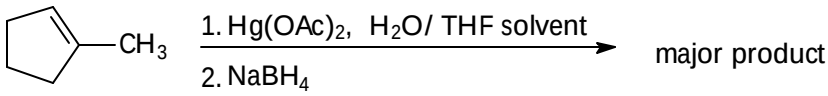
28.

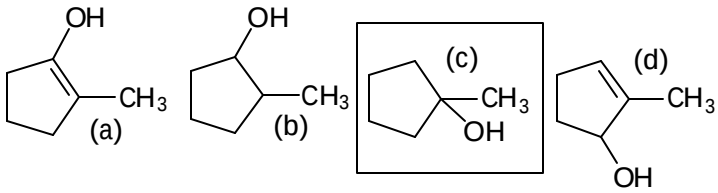




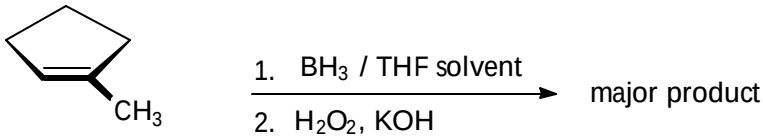
(a) I, <u>(b) II</u>, (c) III, (d) IV, (e) V, (f) II&III, (g) IV&V

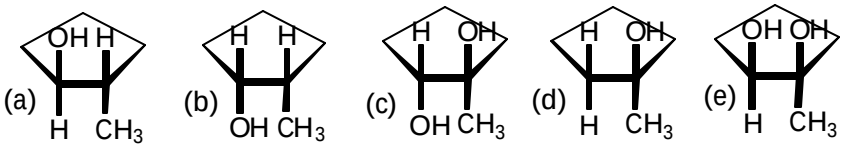
29.





30.



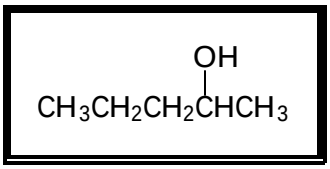


<u>(a) Anti-Markovnikov syn addition of H and OH</u>.

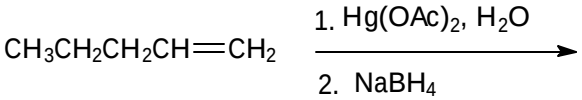
Part II — Write your answers to the following questions in the spaces provided. If there is not enough room continue your answer on the back of the sheet and clearly indicate that you have done this.

1. 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.]

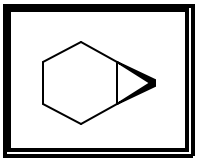
(a) Synthesize 2-pentanol, from a hydrocarbon containing not more than 5 carbons.



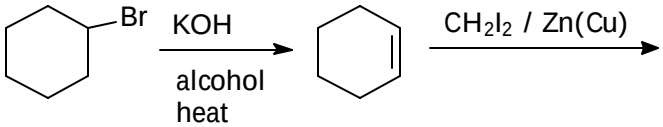
2-pentanol



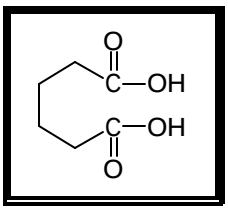
(b) Synthesize bicyclo[4.1.0]heptane starting with bromocyclohexane and employing any other materials you need.



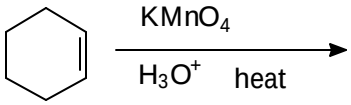
bicyclo[4.1.0] heptane



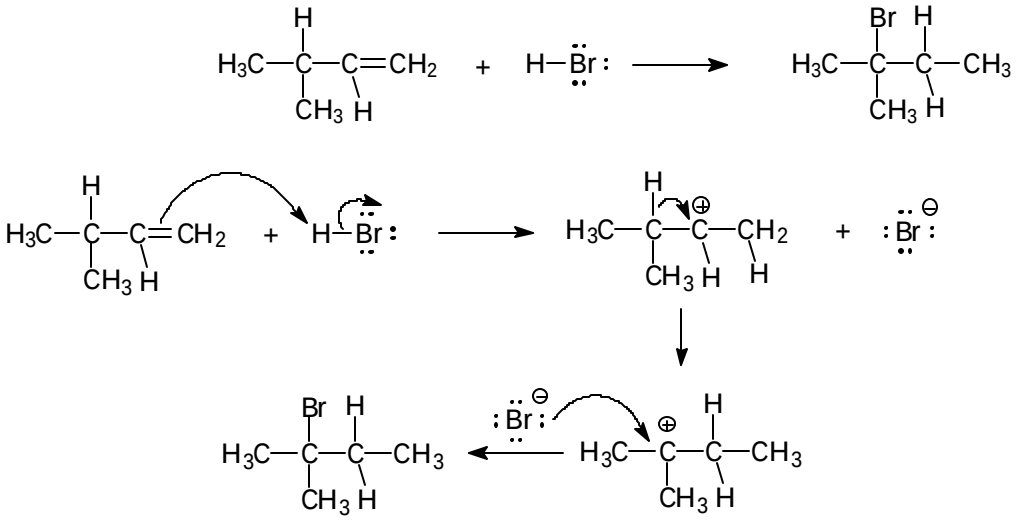
(c) Hexanedioic acid can be used to make Nylon. Your job is to outline a synthesis of hexanedioic acid starting with cyclohexene. You may use any other materials you require.



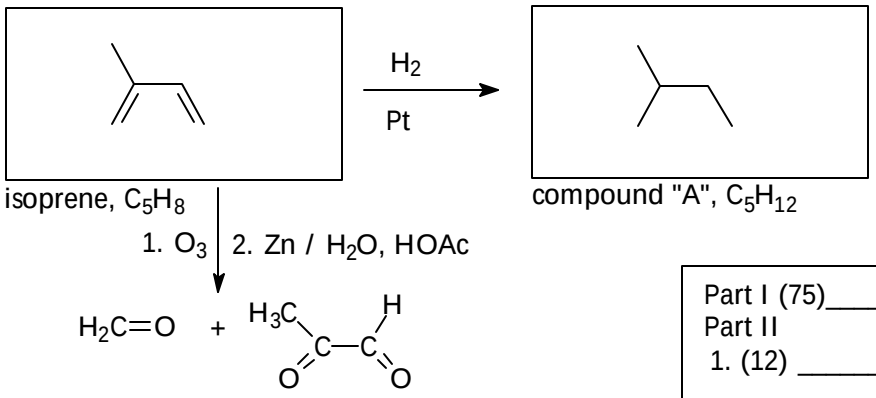
hexanedioic acid



2. Mechanism. Outline all steps in the mechanism of the following reaction. Draw the structures of all intermediates. Use curved arrows to show electron movement. Do not draw structures of transition states. Do not draw a reaction energy diagram.



3. Roadmap. Isoprene is the monomer for the polymer rubber. Its molecular formula is C_5H_8. Upon treatment with hydrogen in the presence of a platinum metal catalyst compound "A" of molecular formula C_5H_{12} is formed. Ozonolysis of isoprene produces the two compounds shown. Draw the structures of isoprene and compound "A".



Part I (75)	_____
Part II	
1. (12)	_____
2. (7)	_____
3. (6)	_____
Total	_____