

Name \_\_\_\_\_

**Department of Chemistry  
SUNY/Oneonta**

**Chem 322 - Organic Chemistry II  
Examination #1 - February 10, 1997**

**INSTRUCTIONS ---**

This examination has two parts. Part I is in multiple choice format and the answers should be placed on the "Test Scoring Answer Sheet" which must be turned in and will be machine graded.

Part II requires your responding to questions by writing answers into the spaces provided in this booklet. This Exam Booklet must be handed in and will be returned to you with a grade. Write your name in the space above NOW.

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 (30032201) and the test number (01); 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 2.4 points each.

You have 90 minutes. Good luck!

1. Which of the following would be the best natural source of aromatic compounds?

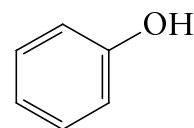
(a) petroleum, (b) bituminous coal, (c) anthracite coal, (d) natural gas

2. Which of the following series of numbers represents the number of  $\pi$ -electrons that could be found delocalized in conjugated monocyclic rings that are aromatic?

(a) 2, 4, 6, 8, ...; (b) 3, 5, 7, 9, ...; (c) 4, 8, 12, 16, ...; (d) 2, 6, 10, 14, ...

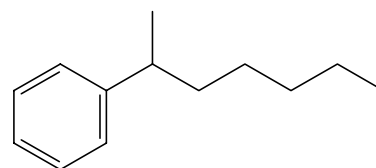
3. The compound shown to the right is known as

(a) toluene, (b) phenol, (c) aniline, (d) benzaldehyde, (e) styrene



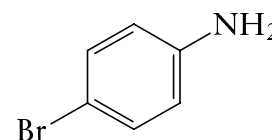
4. The IUPAC name for the compound shown to the right is

(a) 2-benzylheptane. (b) 2-phenylheptane.  
(c) 2-heptylbenzene. (d) 1-methyl-1-phenylhexane.  
(e) 1-methyl-1-benzylhexane.



5. The IUPAC name for the compound shown to the right is

(a) *p*-bromophenol. (b) 3-bromoaniline.  
(c) *p*-bromoaniline. (d) 4-bromoanthracene.  
(e) 4-aminobromobenzene.

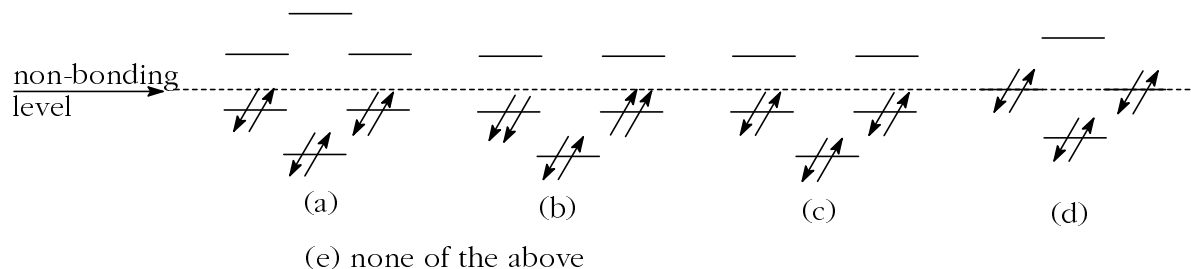


6. The compound shown to the right is known as prismane or Ladenburg benzene. What relationship does this compound bear to benzene?

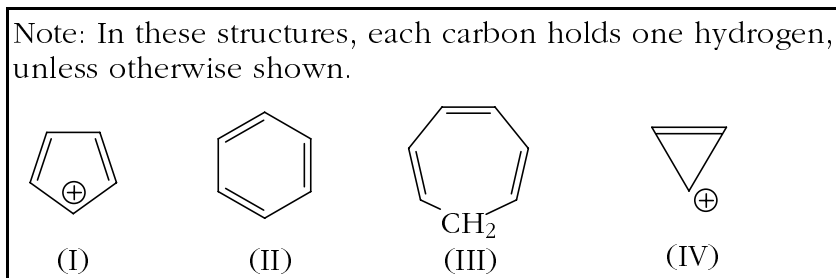
(a) It is a (poor) resonance structure of benzene. (b) It is an enantiomer of benzene.  
(c) It is a diastereomer of benzene. (d) It is a structural isomer of benzene.  
(e) It bears no relationship to benzene.



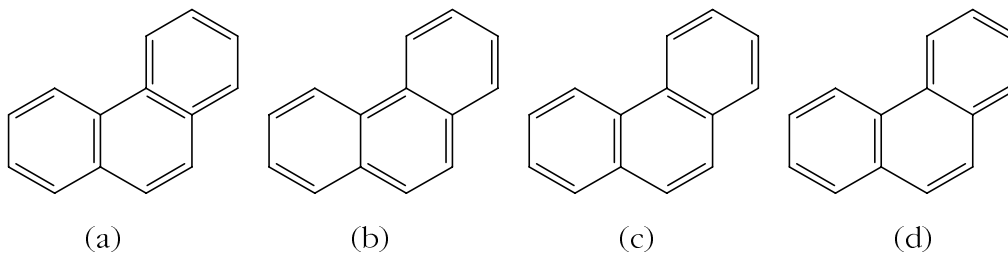
7. Which of the following is a representation of the  $\pi$  molecular orbitals in the cyclopentadienide anion,  $C_5H_5^{-1}$ ?



8. According to simple Huckel theory, which of the following rings should *not* be aromatic?



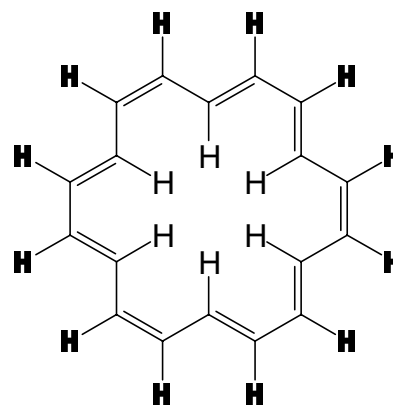
- (a) I & II, (b) II & III, (c) III & IV, (d) I & III, (e) II & IV,  
 (f) None of the above answers is correct.
9. Which of the following is *not* a valid resonance structure for phenanthrene?



10. Benzene is most prone to undergo which of the following?

- (a) electrophilic addition, (b) nucleophilic addition,  
(c) electrophilic substitution, (d) nucleophilic substitution

11. In the proton NMR spectrum of [18]annulene, the structure of which is shown to the right, the interior hydrogens (H) appear at  $-3.0$  ppm (upfield) from TMS, while the exterior hydrogens (H) appear at  $9.3$  ppm (downfield) from TMS. This difference in chemical shift can be explained in terms of

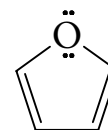


- (a) a steric factor.  
(b) different hybridization of the carbons holding the two different types of hydrogen.  
(c) the interior hydrogens being attached to *trans* double bonds.  
(d) a ring current around the aromatic system.

12. The idea that real benzene is about  $150$  kJ/mol ( $36$  kcal/mol) more stable than the *hypothetical* 1,3,5-cyclohexatriene (which has alternating double and single bonds around the six-member ring, but in which the double bonds are *isolated* from each other) is based on

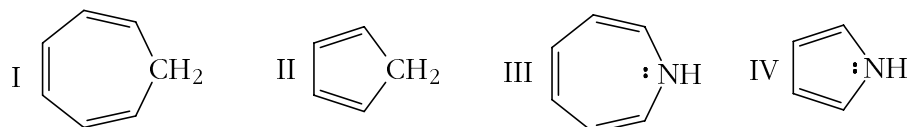
- (a) molecular mechanics calculations. (b) quantum mechanics calculations. (c) heats of hydrogenation of benzene and cyclohexene. (d) the difference in boiling point between benzene and cyclohexene.

13. Assuming that the oxygen atom in furan is  $sp^2$ -hybridized, is this molecule aromatic? Select the correct response below. One of the resonance structures of furan is shown to the right.

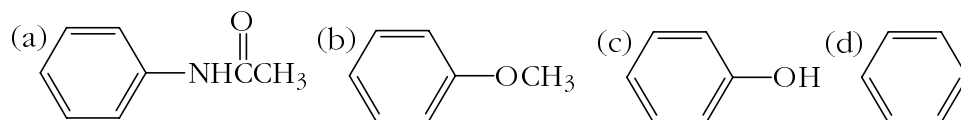


- (a) Yes, it is aromatic;  $4 \pi$  electrons are delocalized around the ring.  
(b) Yes, it is aromatic;  $6 \pi$  electrons are delocalized around the ring.  
(c) Yes, it is aromatic;  $8 \pi$  electrons are delocalized around the ring.  
(d) No, it is not aromatic;  $4 \pi$  electrons are delocalized around the ring.  
(e) No, it is not aromatic;  $6 \pi$  electrons are delocalized around the ring.  
(f) No, it is not aromatic;  $8 \pi$  electrons are delocalized around the ring.

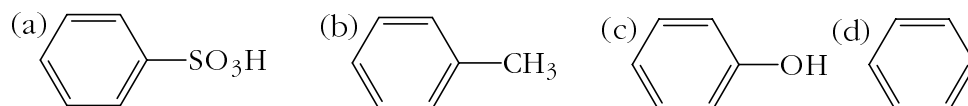
14. Of the compounds shown, list the strongest acid (first) and strongest base (second).



- (a) I, III, (b) I, IV, (c) II, III, (d) II, IV, (e) None of the prior answers is correct.
15. Which of the following statements is *not* true of benzene?
- (a) All the carbon-carbon bonds are of the same length.  
(b) Three and only three isomers of dimethylbenzene (xylene) are possible.  
(c) It has six p-electrons in bonding orbitals.  
(d) All the carbons are sp hybridized.  
(e) It normally undergoes electrophilic substitution in preference to electrophilic addition reactions.
16. Which of the following compounds reacts most slowly with  $\text{HNO}_3/\text{H}_2\text{SO}_4$ ?

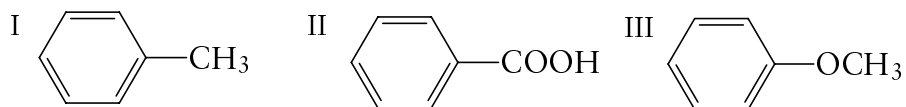


17. Which of the following compounds reacts most rapidly with  $\text{HNO}_3/\text{H}_2\text{SO}_4$ ?



18. Rank the following three compounds in order of decreasing reactivity toward ring bromination (most reactive first).

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



19. Again consider the three compounds in question #18. Select the answer that correctly indicates the major products that would be obtained by monobromination of the rings.

Answer	ortho + para isomers	meta isomer
(a)	I	II & III
(b)	I & II	III
(c)	I, II & III	(none)
(d)	(none)	I, II & III
(e)	I & III	II

20. Which of the following compounds would not be a good candidate for providing the ethyl group in an alkylation reaction that would convert benzene to ethylbenzene.

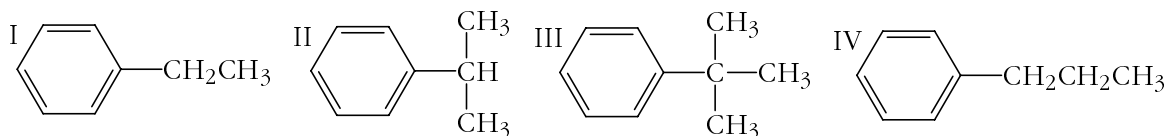
- (a) ethane, (b) ethylene, (c) ethanol, (d) chloroethane.

21. Predict the major monoalkylation products you would expect to obtain from reaction of each of the following substances with chloromethane and anhydrous  $\text{AlCl}_3$ .

I: *p*-chloroaniline. II: 2,4-dichlorophenol.

- (a) I  $\rightarrow$  *p*-methylaniline; II  $\rightarrow$  2,4-dichloro-5-methylphenol.  
 (b) I  $\rightarrow$  4-chloro-3-methylaniline; II  $\rightarrow$  2,4-dichloro-6-methylphenol.  
 (c) I  $\rightarrow$  4-chloro-2-methylaniline; II  $\rightarrow$  2,4-dichloro-5-methylphenol.  
 (d) I  $\rightarrow$  no reaction; II  $\rightarrow$  2,4-dichloro-6-methylphenol.

22. Consider the four compounds shown below. Which of these compounds could not be synthesized in good yield by carrying out a Friedel-Crafts *alkylation* on benzene?



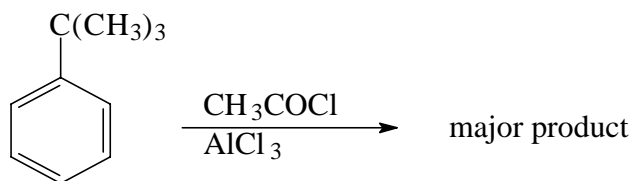
- (a) I, (b) II, (c) III, (d) IV, (e) I&IV, (f) II&III, (g) II-IV
23. Consider the four compounds shown in question #22. Which of these compounds could not be synthesized in good yield by carrying out a Friedel-Crafts *acylation* on benzene, followed by an appropriate reduction?

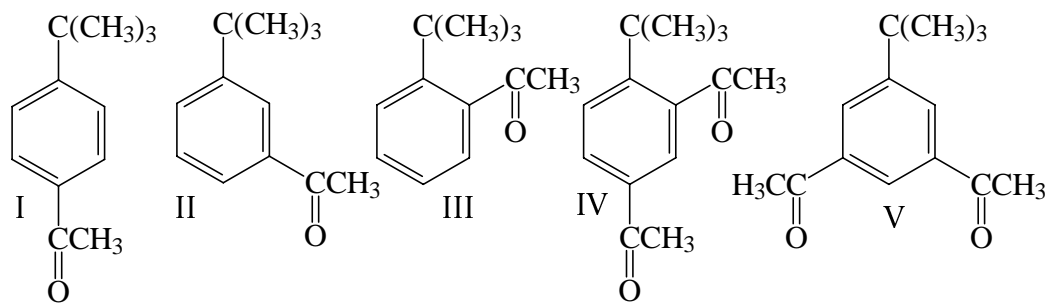
(a) I, (b) II, (c) III, (d) IV, (e) I&IV, (f) II&III, (g) II-IV

24. What is the electrophile in the desulfonation reaction of benzenesulfonic acid to give benzene?

(a)  $\text{H}^+$  or  $\text{H}_3\text{O}^+$ , (b) benzene, (c) water, (d)  $\text{Ph-SO}_3^-$ , (e)  $\text{SO}_3$

- 25.

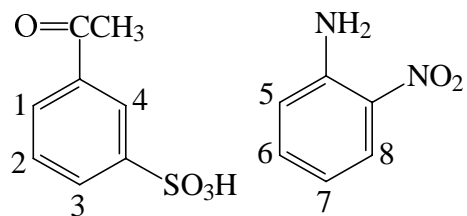




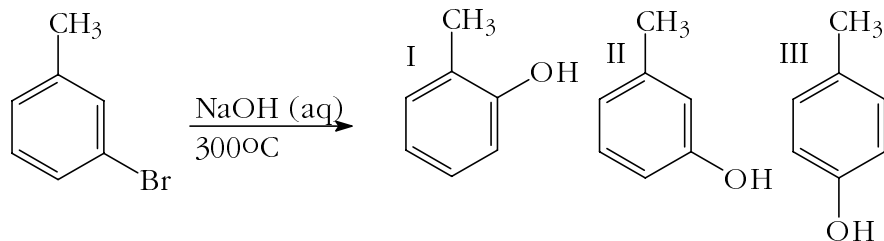
(a) I, (b) II, (c) III, (d) IV, (e) V, (f) no reaction

26. Which positions in these molecules would be good sites for electrophilic substitution?

(a) 1,3,4,5,6,7,8, (b) 2,5,7, (c) 1,3,5,7,  
(d) 2,4,5,8, (e) 1,2,3,4,5,6,7



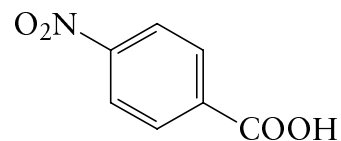
27. Which products would actually form in the reaction shown to the right?



(a) I, (b) II,  
(c) III,  
(d) I & II,  
(e) I & III,  
(f) I, II & III, (g) There would be no reaction.



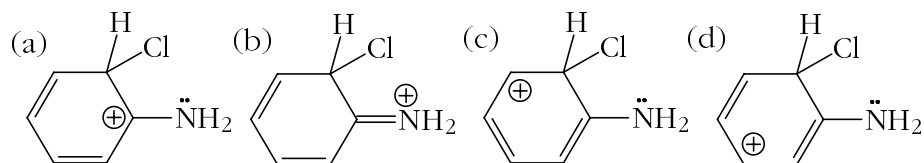
28. Which of the following synthetic procedures would be likely to be successful in making *p*-nitrobenzoic acid from benzene?



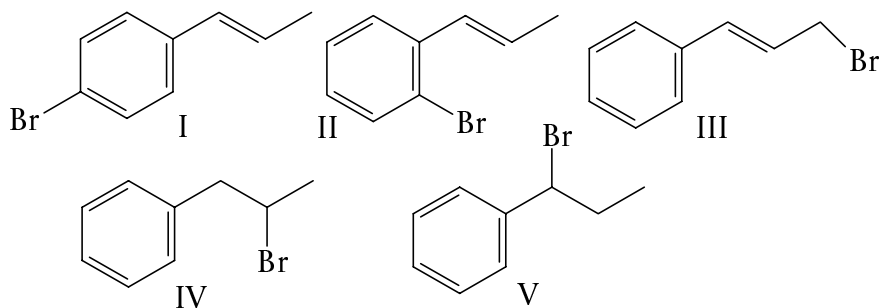
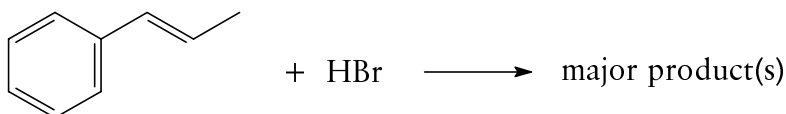
- (I) (1)  $\text{HNO}_3/\text{H}_2\text{SO}_4$ , (2)  $\text{HCOOH}/\text{KOH}$ .  
 (II) (1)  $\text{HNO}_3/\text{H}_2\text{SO}_4$ , (2)  $\text{CH}_3\text{Br}/\text{AlCl}_3$ , (3)  $\text{KMnO}_4/\text{heat}$ .  
 (III) (1)  $\text{HCOOH}/\text{KOH}$ , (2)  $\text{HNO}_3/\text{H}_2\text{SO}_4$ .  
 (IV) (1)  $\text{CH}_3\text{Br}/\text{AlCl}_3$ , (2)  $\text{HNO}_3/\text{H}_2\text{SO}_4$ , (3)  $\text{KMnO}_4/\text{heat}$ .  
 (V) (1)  $\text{CH}_3\text{Br}/\text{AlCl}_3$ , (2)  $\text{KMnO}_4/\text{heat}$ , (3)  $\text{HNO}_3/\text{H}_2\text{SO}_4$ .

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

29. Which of the following resonance structures is *most* important to the stability of the intermediate that is formed when aniline undergoes electrophilic attack in ring chlorination at a position *ortho* to the  $\text{NH}_2$  group?



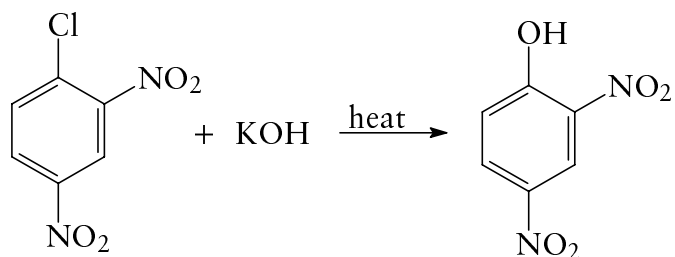
30.



Answers

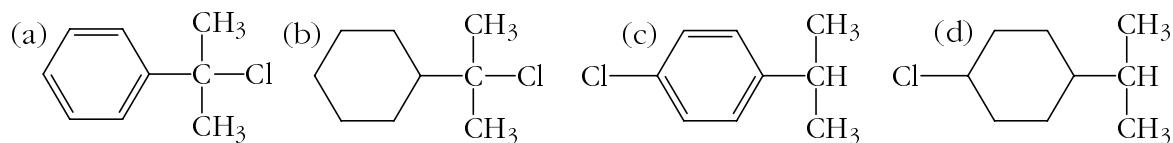
- (a) I&II,  
 (b) III,  
 (c) IV  
 (d) V  
 (e) IV&V

31.



The mechanism for the above reaction involves

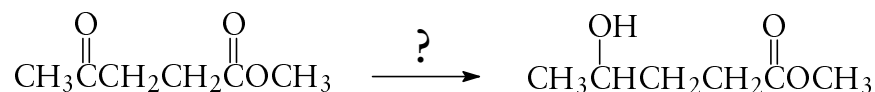
- (a)  $S_N1$  substitution of Cl by OH.  
 (b)  $S_N2$  substitution of Cl by OH.  
 (c) an elimination-addition sequence involving a substituted benzyne as an intermediate.  
 (d) nucleophilic attack by  $\text{OH}^-$  at the chlorine-bearing carbon, resulting in the formation of a carbanion that subsequently loses  $\text{Cl}^-$ .  
 (e) electrophilic attack by  $\text{OH}^-$  at the chlorine-bearing carbon, resulting in the formation of a carbocation that subsequently loses  $\text{Cl}^-$ .
32. The purpose of the anhydrous aluminum chloride catalyst in the Friedel-Crafts alkylation is to
- (a) form a reactive complex with the benzene ring.  
 (b) donate a pair of electrons to the alkyl halide.  
 (c) accept a pair of electrons from the halogen of the alkyl halide.  
 (d) assist in the removal of a proton from the intermediate in the reaction.
33. A mixture of equimolar amounts of isopropylbenzene, isopropylcyclohexane, and NBS (N-bromosuccinimide) is exposed to UV light. What is the major organic product isolated from the reaction mixture?



34. Which method is most satisfactory for the conversion of 1-butene into 1-butanol?

- (a) Reaction with water and sulfuric acid.  
 (b) Reaction with water and  $\text{H}_3\text{BO}_3$ .  
 (c) Reaction with  $\text{B}_2\text{H}_6$ , then water and potassium hydroxide.  
 (d) Reaction with  $\text{B}_2\text{H}_6$ , then hydrogen peroxide and potassium hydroxide.  
 (e) Reaction with  $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}$ , then  $\text{NaBH}_4$ .

35. What reagent(s) would you use to accomplish the following reaction?



- (a)  $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ , (b) (1)  $\text{LiAlH}_4$ , (2)  $\text{H}_3\text{O}^+$ , (c) (1)  $\text{NaBH}_4$ , (2)  $\text{H}_3\text{O}^+$ ,  
 (d) (1)  $\text{B}_2\text{H}_6$ , (2)  $\text{H}_2\text{O}_2/\text{KOH}$ , (e)  $\text{H}_2/\text{Pd}$

36. Which of the following compounds can be reduced with lithium aluminum hydride to give 2-methyl-1-propanol,  $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ ?

I:  $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$ , II:  $(\text{CH}_3)_2\text{CHCH}=\text{O}$ , III:  $(\text{CH}_3)_2\text{CHCOOH}$ , IV:  $(\text{CH}_3)_2\text{C}=\text{CH}_2$

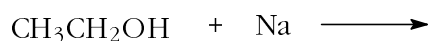
- (a) I&II, (b) II&III, (c) III&IV, (d) II&IV, (e) I&III

37. Arrange the following compounds in order of decreasing acidity (most acidic first).

I:  $\text{CH}_2\text{CH}_2\text{OH}$ , II:  $\text{H}-\text{C}\equiv\text{C}-\text{H}$ , III:  $\text{CH}_3\text{CH}_3$ , IV:  $\text{CH}_3\text{COOH}$ , V:  $\text{C}_6\text{H}_5-\text{SO}_3\text{H}$

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

38. Select the major product(s) of the following reaction.



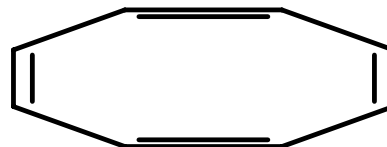
- (a)  $\text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+ + \text{H}_2$  (b)  $\text{CH}_3\overset{\text{O}}{\parallel}\text{CH} + \text{NaH}$  (c)  $\text{Na}^+ \text{CH}_2\text{CH}_2\text{OH}^- + \text{H}_2$

- (d)  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{NaOH} + \text{H}_2$  (e) No reaction takes place.

39. Which product would be formed, after workup with dilute sulfuric acid, when an excess of phenylmagnesium bromide, Ph-Mg-Br, reacts with methyl benzoate, PhCOOCH<sub>3</sub>?
- (a) Ph<sub>3</sub>C-OH, (b) Ph<sub>2</sub>CH-OH, (c) Ph-CO-Ph, (d) Ph<sub>3</sub>CH,  
(e) Bogus query! Phenylmagnesium does not react with esters.
40. Which of the following procedures could be used to prepare a secondary (2°) alcohol?
- I: Reduction of an aldehyde. II: Reduction of a ketone. III: Reduction of a carboxylic acid. IV: A Grignard synthesis using formaldehyde. V: A Grignard synthesis using an aldehyde other than formaldehyde. VI: A Grignard synthesis using a ketone.
- (a) I, III, V, (b) II, IV, V, VI, (c) II, V, (d) I, II, III,  
(e) None of the above answers is correct.
41. Which of the following functional groups cannot be present in a halogen-containing compound you wish to react with magnesium to form a Grignard reagent?
- I: -COOH, II: -COCH<sub>3</sub>, III: -NO<sub>2</sub>
- (a) I, (b) II, (c) III, (d) I&II, (e) I&III, (f) II&III, (g) I - III,  
(h) Yo! Bogus question! Any of those three groups could be present.
42. Which of the following reagents would be most successful at converting 1-butanol to butanal, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=O?
- (a) KMnO<sub>4</sub>, (b) CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>, (c) Na<sub>2</sub>CrO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub>, (d) C<sub>5</sub>H<sub>6</sub>NCrO<sub>3</sub>Cl/CH<sub>2</sub>Cl<sub>2</sub>

**Part II. Enter your answers in the space provided. If there is inadequate room, continue on the back of the page and clearly indicate on the front of the page that you have done this. Hand in this entire exam booklet when you are finished; it will be returned to you with your grade. Make sure your name is on the front sheet.**

1. **Theory.** With regard to its chemical behavior 1,3,5,7-cyclooctatetraene acts like an ordinary alkene (with four double bonds). It exhibits neither special stability, nor special instability.

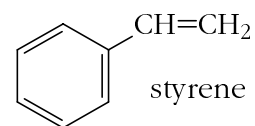


(a) Using simple molecular orbital theory, or rules derived therefrom, predict whether this molecule should be aromatic or antiaromatic. [If you want credit for your answer, show clearly how you arrived at your answer from the theory or rules.]

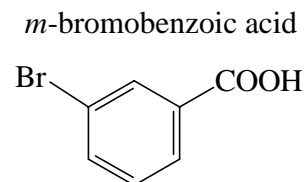
(b) Explain why this molecule is essentially an ordinary alkene in spite of the prediction made in part (a).

2. **Synthesis.** Draw an outline for each of the following syntheses. Show all materials and any special conditions employed as you write the reactions which constitute your outline. Do not balance equations or show mechanisms.

(a) Starting with benzene, and using any other materials you need, synthesize styrene.



(b) Starting with benzene, and using any other materials you need, synthesize *m*-bromobenzoic acid.



(c) Starting with benzene, and using any other materials you need, outline a Grignard synthesis of 2-phenyl-2-butanol.

(d) Convert 1-bromobutane into 2-butanol in good yield, using any needed materials.

3. **Mechanism.**

- (a) Show the mechanism for the reaction shown below. Draw all important resonance structures of the intermediate  $\sigma$ -complex and indicate which makes the greatest contribution. Do not show transition states.



- (b) If the reaction in part (a) is carried out at 80°C instead of 0°C, *m*-xylene is the principal product, not *o*- or *p*-xylene. Explain why *o*- and *p*-xylene are the principal products at a low temperature and *m*-xylene is the major product at a higher temperature.

Part I (100) _____
Part II
1. (5) _____
2. (15) _____
3. (5) _____
Total (125) _____

 **Please return the pencil.** 