

Name _____

Department of Chemistry
SUNY/Oneonta

Chem 322 - Organic Chemistry II
Examination #1 - February 10, 2003 **ANSWERS**

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 OSC student (or 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. (If you use your OSC Student number, enter the whole number including the prefix letter but do not darken any bubbles under the letter.)

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!

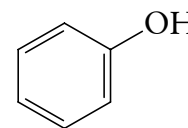
Answers are highlighted in red.

Explanations are in red type.

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. In chemical terms, an aromatic compound is one that
(a) smells sweet. (b) smells putrid. (c) has a pleasant smell. (d) smells.
(e) has chemical properties similar to those of benzene.
3. Which of the following series of numbers represents the number of π -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, ...

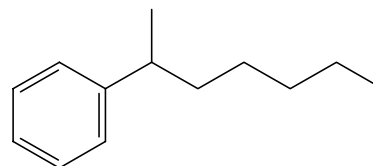
numbers = $4n+2$, where n is 0, 1, 2, 3 ...

4. The compound shown to the right is known as
(a) toluene, (b) phenol, (c) aniline, (d) phenyl, (e) styrene



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

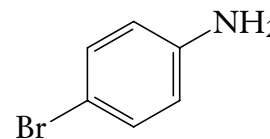
- (a) 2-benzylheptane. (b) 2-phenylheptane.
(c) 2-heptylbenzene. (d) 1-methyl-1-phenylhexane.
(e) 1-methyl-1-benzylhexane.



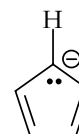
The alkyl group has more carbons than the benzene ring so the alkyl group becomes the parent.

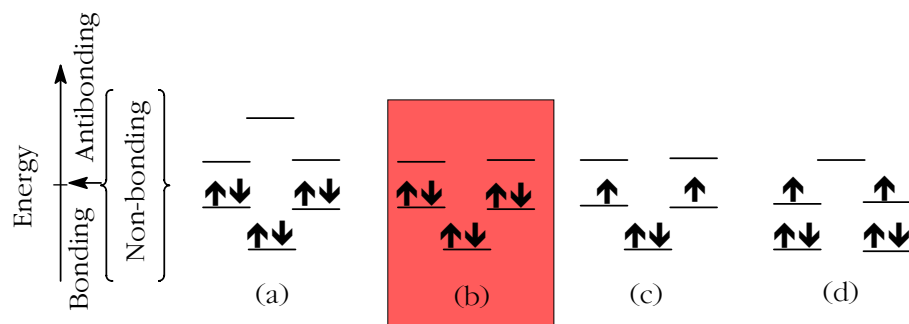
6. A correct name for the compound shown to the right is

- (a) *p*-bromophenol. (b) 3-bromoaniline.
(c) *p*-bromoaniline. (d) 4-bromoanthracene.
(e) None of the above names is correct.



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

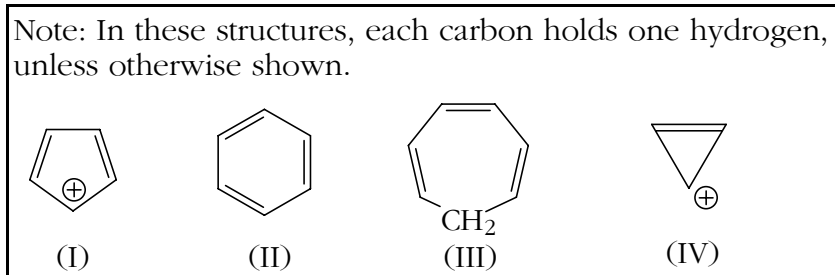




(d) None of the above answers is correct.

In a potentially aromatic monocyclic ring system the energy levels of the π molecular orbitals can be obtained by drawing the polygon that represents the molecule (in this case a pentagon) with one apex pointing down. The energy levels then correspond to the apexes of the polygon. The center of the polygon corresponds to the non-bonding energy level (there may or may not be non-bonding orbitals in the molecule; in this case there are not); orbitals below this level are bonding, above it they are antibonding. This anion has 6 π electrons; they fill the orbitals as shown.

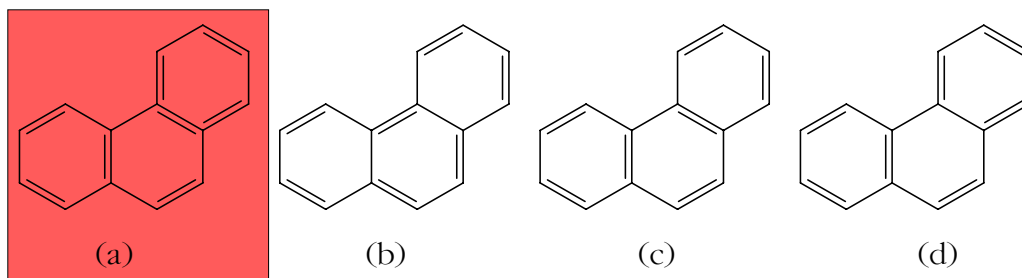
8. Which of the following rings should *not* be aromatic?



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

III has a carbon in the ring that is not a π -center (CH_2 is sp^3 hybridized). For I, II and IV to be aromatic they must fit the $4n+2$ rule; I doesn't but II and IV do.

9. Which of the following is *not* a valid resonance structure for phenanthrene?

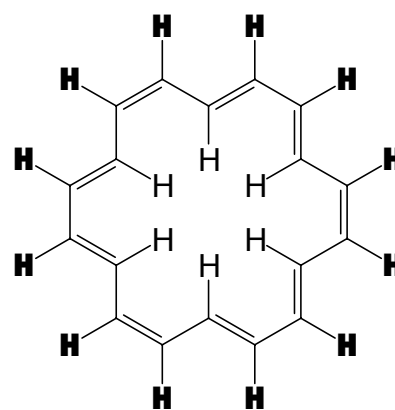


(a) has two too many π electrons. It also has two pentavalent carbons.

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.

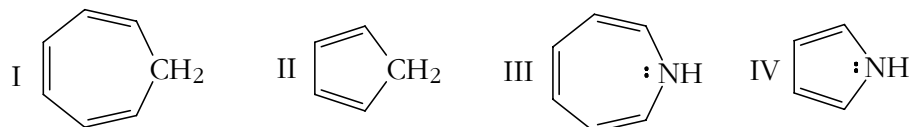
(d) a ring current around the aromatic system.

See page 580 in McMurry, 5th edition.

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. Of the two hydrocarbons (I&II) shown, list the stronger acid (first) and of the two heterocycles (III&IV) list the stronger base (second).



- (a) I, III, (b) I, IV, (c) II, III, (d) II, IV, (e) Bogus question, dude! None of these compounds is acidic or basic.

If II gives up a proton at CH₂, leaving the pair of electrons in the C-H bond on the ring, the ring has 6 π electrons; it is aromatic. Therefore, the proton is given up relatively easily. If I gives up a proton at CH₂, leaving the pair of electrons in the C-H bond on the ring, the ring has 8 π electrons; it is anti-aromatic. Therefore, the proton is not given up easily.

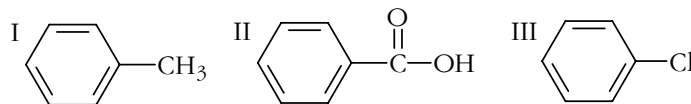
In IV the electron pair shown on N is actually delocalized around the ring, along with the other 4 π electrons, to form a 6 π electron aromatic ring: pyrrole. For this compound to act as a base it would have to donate this pair of electrons to form a bond to an acid; this breaks up the aromatic character of the ring so it doesn't happen easily. On the other hand, if the pair of electrons shown on the N in III (azepine) were delocalized around the ring, this compound would be anti-aromatic (8 π electrons); therefore, this compound has no incentive for this to happen and donating them to form a bond to an acid is a good alternative. I might note in passing that, to my knowledge, azepine itself has never been made, but derivatives of it have been made and the ring adopts a non-planar conformation (like 1,3,5,7-cyclooctatetraene). This baby wants to avoid being anti-aromatic.

14. 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, not counting conformational isomers.
 (c) It has six π -electrons in bonding orbitals.
 (d) All the carbons are sp² hybridized.
 (e) Its carbons and hydrogens lie in a common plane.
 (f) Bogus question, dude. All of the above statements are true.

15. 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



Memorize the list. :^)

16. Again consider the three compounds in question #15. 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

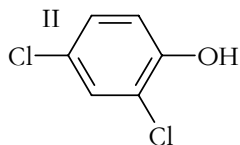
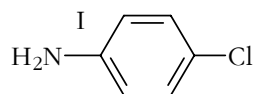
Memorize the list. :^)

17. Which of the following compounds would not be a good candidate for providing the ethyl group in a Friedel-Crafts type alkylation reaction that would convert benzene to ethylbenzene.

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

It is possible to generate something that looks like a carbocation from (b) thru (d), by use of an acid, but not from (a).

18. Predict the major monoalkylation products you would expect to obtain from reaction of each of the following substances with chloromethane and anhydrous AlCl_3 .



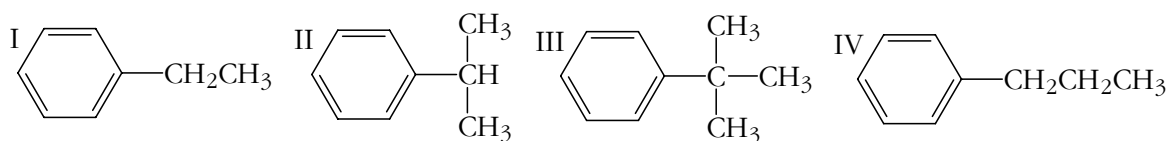
- (a) I \rightarrow *p*-methylaniline; II \rightarrow 2,4-dichloro-5-methylphenol.
 (b) I \rightarrow 4-chloro-3-methylaniline; II \rightarrow 2,4-dichloro-6-methylphenol.
 (c) I \rightarrow 4-chloro-2-methylaniline; II \rightarrow 2,4-dichloro-5-methylphenol.

- (d) I \rightarrow no reaction; II \rightarrow 2,4-dichloro-6-methylphenol.**

I: Anhydrous aluminum chloride is a powerful Lewis acid and the $-\text{NH}_2$ group is a good Lewis base. The $-\text{NH}_2$ group donates its unshared pair of electrons to form a bond to aluminum. This places a positive charge on the nitrogen, making it a powerful deactivating group for the benzene ring. This is why aniline compounds are a no go for Friedel-Crafts reactions.

II: This $-\text{OH}$ group is a powerful activating group and an ortho/para director; the Cl atoms are weak deactivators. Strong activators usually win out over weak deactivators.

19. 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

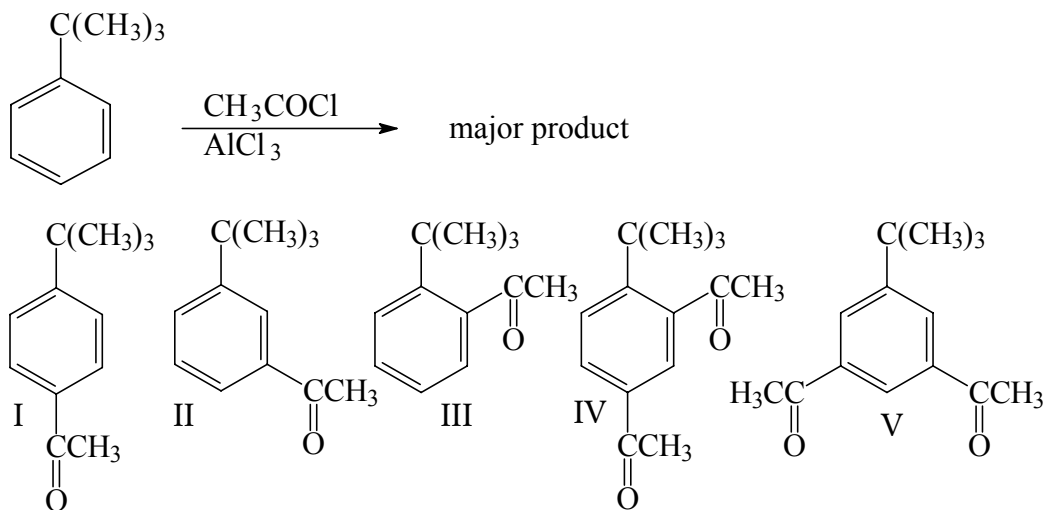
An attempt to make IV would also produce II via a rearrangement of the carbocation-like intermediate.

20. Consider the four compounds shown in question #19. 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 of the ketone obtained?

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

This method results in a $-\text{CH}_2-$ group next to the ring; II and III do not fit this pattern.

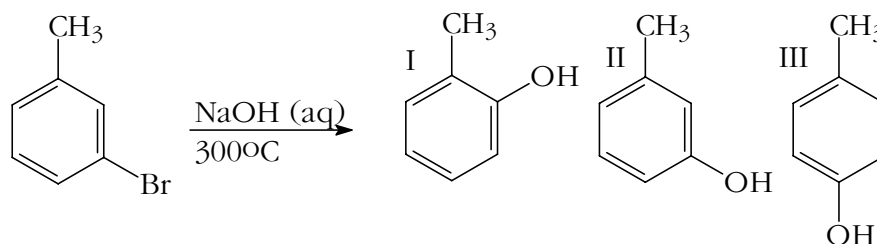
21.



(a) I, (b) II, (c) III, (d) IV, (e) V, (f) Bogus question, dude. There would be no reaction.

The *t*-butyl group is an alkyl group and alkyl groups electronically direct incoming electrophiles to the ortho and para positions. However, *t*-butyl is a bulky group and, consequently, steric interference between it and the incoming electrophile results in little ortho product being formed.

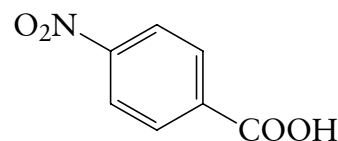
22. Which products would actually form in the reaction shown to the right?



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

Since there are no strong electron withdrawing groups ortho or para to the -Br, the nucleophilic substitution will occur through an elimination - addition sequence (benzyne). This mechanism would lead to all three products.

23. Which of the following synthetic procedures would be likely to be successful in making *p*-nitrobenzoic acid from benzene?
 [Note: (1) = first step, (2) = second step, *etc.*]

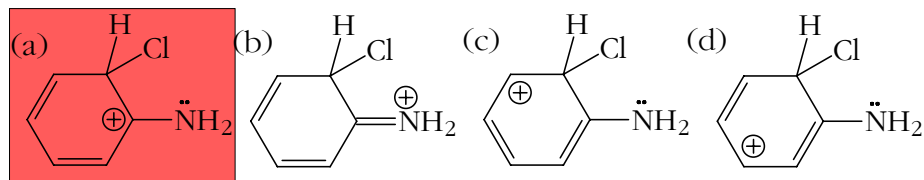


- (I) (1) HNO₃/H₂SO₄, (2) HCOOH/KOH.
 (II) (1) HNO₃/H₂SO₄, (2) CH₃Br/AlCl₃, (3) KMnO₄/heat.
 (III) (1) HCOOH/KOH, (2) HNO₃/H₂SO₄.
 (IV) (1) CH₃Br/AlCl₃, (2) HNO₃/H₂SO₄, (3) KMnO₄/heat.
 (V) (1) CH₃Br/AlCl₃, (2) KMnO₄/heat, (3) HNO₃/H₂SO₄.

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

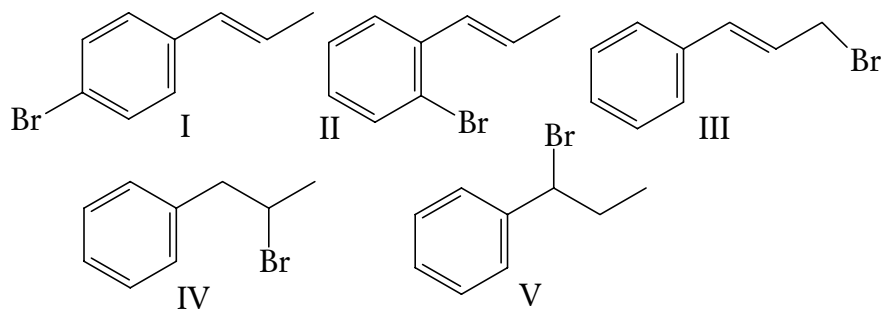
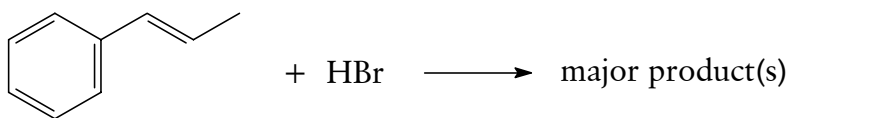
Methyl goes on first to provide *o/p* director. NO₂ goes on ortho (an unavoidable loss) and para. Oxidation of -CH₃ produces the carboxylic acid. HCOOH is bogus. Nitrate the ring first (II) and Fiedel-Crafts doesn't work. Convert the -CH₃ to -COOH before nitration (V) and the -NO₂ goes meta.

24. Which of the following resonance structures is *least* important to the stability of the intermediate that is formed when aniline undergoes electrophilic attack in ring chlorination at a position *ortho* to the NH₂ group?



Nitrogen is an electronegative element and so inductively withdraws electrons from the positively charged ring carbon – not good.

25.



Answers

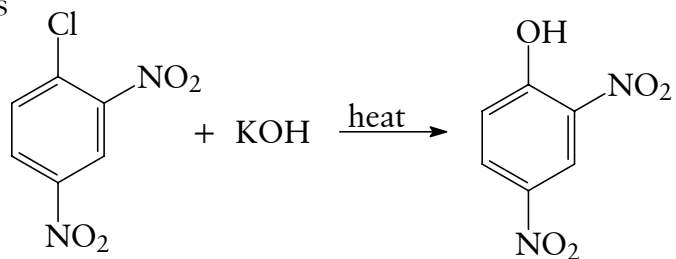
- (a) I&II,
 (b) III,
 (c) IV
 (d) V
 (e) IV&V

(d)

IV and V are the only reasonable answers. The carbocation leading to IV is 2°; the one leading to V is 2° and benzylic (more stable than just 2°).

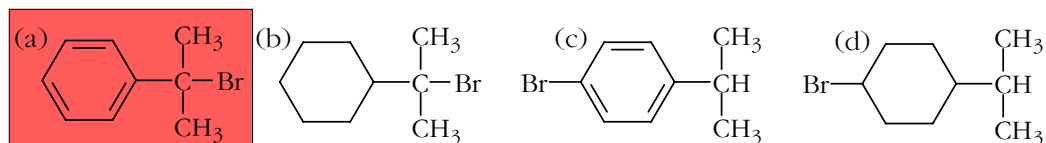
26. The mechanism for this reaction involves

- (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.



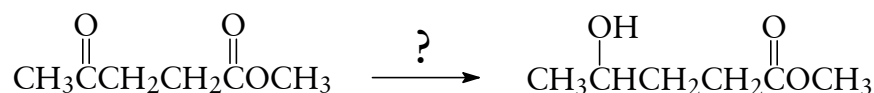
- (d) nucleophilic attack by OH^- at the chlorine-bearing carbon, resulting in the formation of a carbanion that subsequently loses Cl^- .
 (e) electrophilic attack by OH^- at the chlorine-bearing carbon, resulting in the formation of a carbocation that subsequently loses Cl^- .

27. 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?



This is an example of free radical substitution of a benzylic hydrogen by Br.

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



- (a) $\text{H}_3\text{O}^+/\text{H}_2\text{O}$, (b) (1) LiAlH_4 , (2) H_3O^+ , (c) (1) NaBH_4 , (2) H_3O^+ ,
 (d) (1) B_2H_6 , (2) $\text{H}_2\text{O}_2/\text{KOH}$, (e) H_2/Pd

The idea here is to reduce the ketone to an alcohol without reducing the ester; procedure (b) would reduce the ester also. Procedure (e) might reduce an aryl ketone, but this is not an aryl ketone.

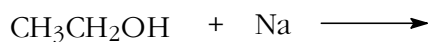
29. Which of the following compounds can be reduced with lithium aluminum hydride to give 2-methyl-1-propanol, $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$?

- I: $(\text{CH}_3)_2\text{CHCH}_3$, 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

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

- I: $\text{CH}_2\text{CH}_2\text{OH}$, II: $\text{C}_6\text{H}_5\text{-OH}$, III: CH_3CH_3 , IV: CH_3COOH , 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. V>IV>II>I>III is correct.

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



- (a) $\text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+ + \text{H}_2$ (b) $\text{CH}_3\text{C}(=\text{O})\text{H} + \text{NaH}$ (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.

(a)

32. Which product would be formed, after workup with dilute sulfuric acid, when an excess of phenylmagnesium bromide, Ph-Mg-Br, reacts with methyl benzoate, PhCOOCH₃?

- (a) Ph₃C-OH, (b) Ph₂CH-OH, (c) Ph-CO-Ph, (d) Ph₃CH,
 (e) Bogus query! Phenylmagnesium does not react with esters.

This is the Grignard synthesis you performed in the lab in Chem 221. :^)

33. 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.

I, III and IV lead to a 1° alcohol. VI leads to a 3° alcohol.

34. 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: -COCH₃, III: -OH

- (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.

I and III are too acidic; they would destroy the Grignard or prevent its formation. II would react with the Grignard as it formed.

35. Which of the following reagents would be most successful at converting 1-butanol to butanal, CH₃CH₂CH₂CH=O?

- (a) KMnO₄, (b) CrO₃/H₂SO₄, (c) Na₂CrO₄/H₂SO₄, (d) C₅H₆NCrO₃Cl/CH₂Cl₂

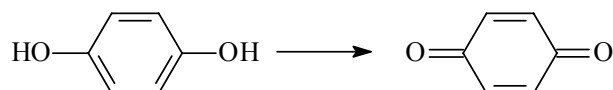
36. The -OH group in phenol is more acidic than that in ethanol. This is mainly the result of
- (a) resonance stabilization that exists in phenol and not in ethanol.
 - (b) resonance stabilization that exists in ethanol and not in phenol.
 - (c) resonance stabilization that exists in the phenoxide anion and not in the ethoxide anion.
 - (d) resonance stabilization that exists in the ethoxide anion and not in the phenoxide anion.

While one can draw five resonance structures for phenol and phenoxide, three of the phenol structures have charge separation; none of the phenoxide structures have charge separation. Neither ethanol nor ethoxide have more than one decent Lewis structure.

37. An electron-withdrawing group attached to the ring of a phenol or to a carbon near the -OH group of an alcohol will
- (a) decrease the acidity of both.
 - (b) increase the acidity of both.
 - (c) decrease the acidity of the alcohol but increase the acidity of the phenol.
 - (d) decrease the acidity of the phenol but increase the acidity of the alcohol.

The electron withdrawing group stabilizes the anion formed from each acid.

38. The reaction to the right represents



- (a) the oxidation of hydroquinone to *p*-benzoquinone.
- (b) the oxidation of *p*-benzoquinone to hydroquinone.
- (c) the reduction of hydroquinone to *p*-benzoquinone.
- (d) the reduction of *p*-benzoquinone to hydroquinone.

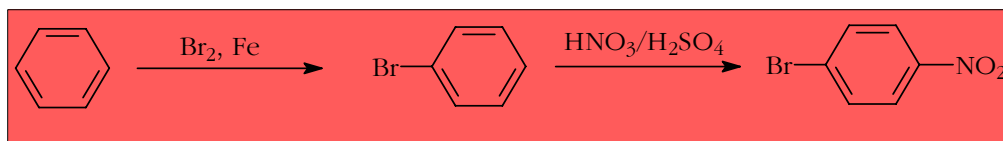
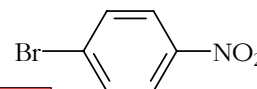
Do Not Detach The Following Sheets From The Rest Of The Exam

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. Do not pass go. Do not collect two-hundred dollars.

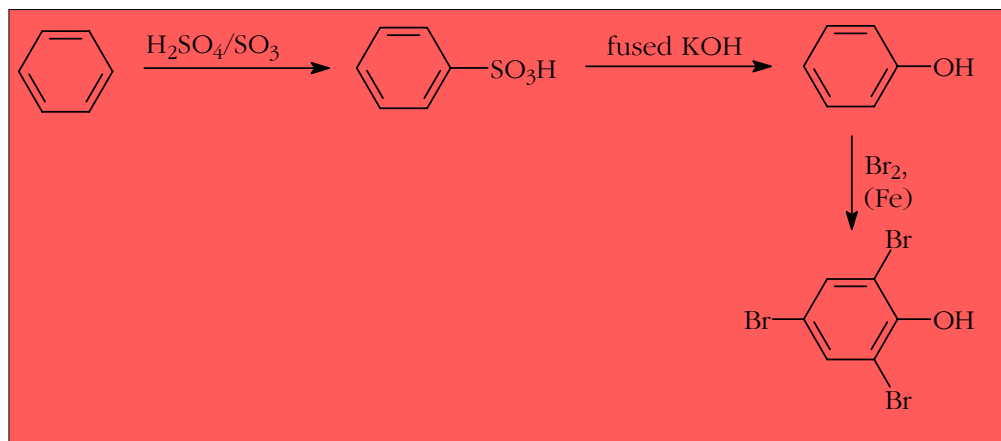
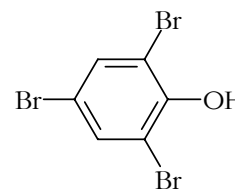
1. **Synthesis.** Draw an outline for each of the following syntheses. Show all materials and any special conditions employed as you write the reactions which constitute your outline. Do not balance equations or show mechanisms.

(a) Starting with benzene and using any other materials you require, outline a synthesis of *p*-nitrobromobenzene.



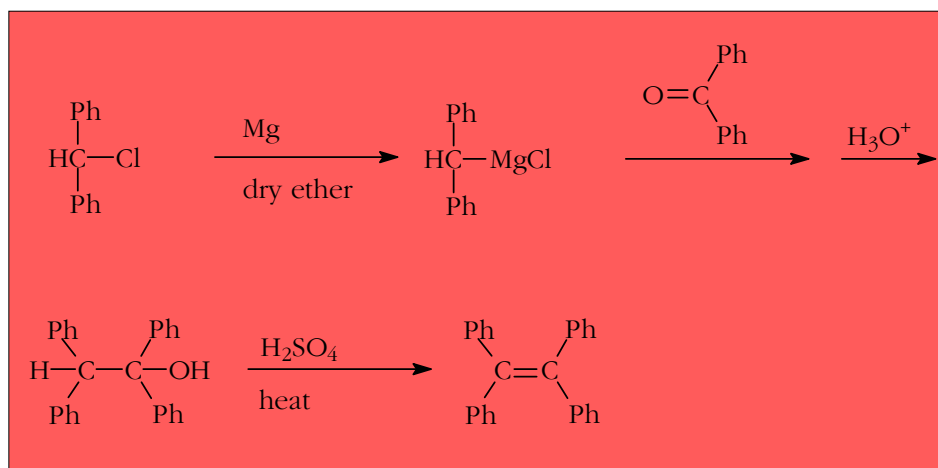
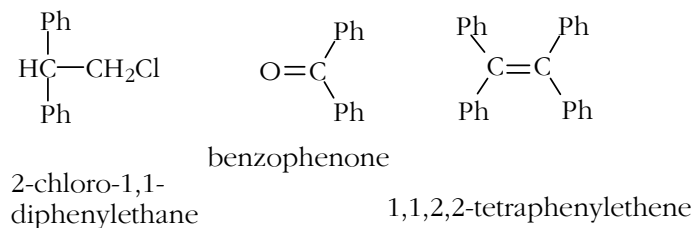
Bromination first, nitration second. The reverse order would lead to *m*-bromonitrobenzene.

(b) Starting with benzene and using any other materials you require, outline a synthesis of 2,4,6-tribromophenol.



Iron to provide the FeCl_3 catalyst may not be necessary in the last step. $-\text{OH}$ is a powerful activating, ortho/para directing, group. On the other hand, as the bromines become attached to the ring they deactivate it to some extent. So, the catalyst may be helpful in allowing the last bromine to become attached.

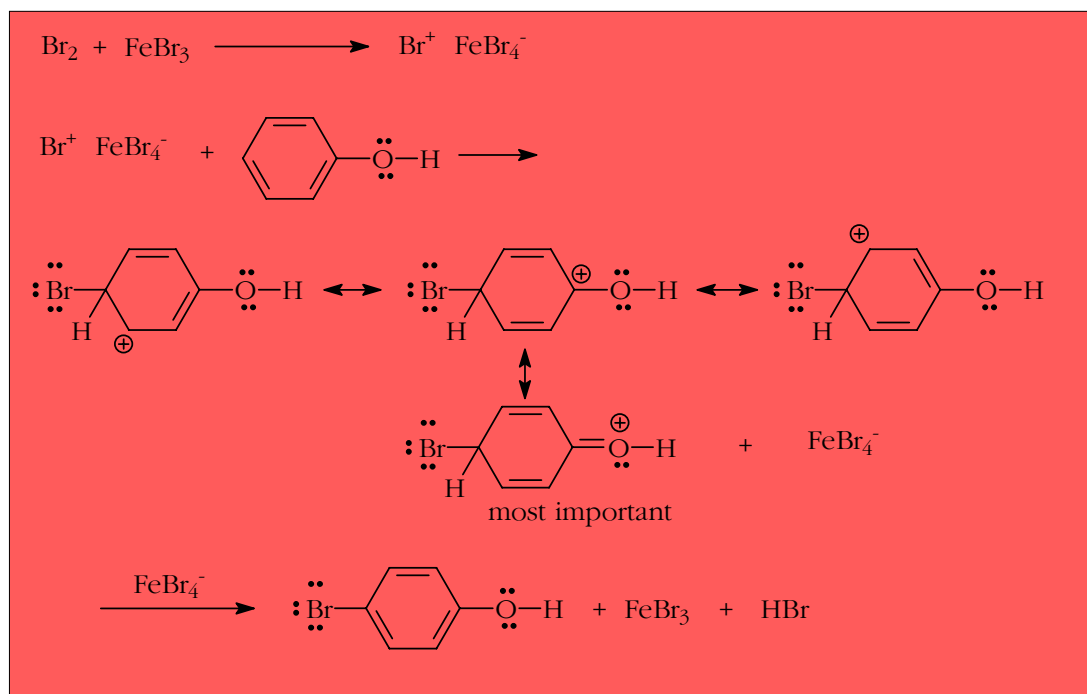
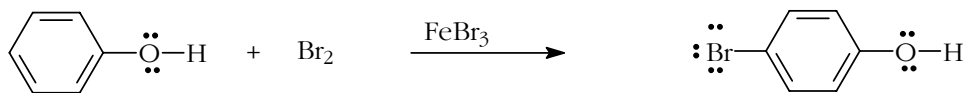
(c) Starting with 2-chloro-1,1-diphenylethane and benzophenone, outline a synthesis of 1,1,2,2-tetraphenylethene. You must employ a Grignard synthesis as part of your procedure.



There was an error in this question. The halide starting material should have been chlorodiphenylmethane and not 2-chloro-1,1-diphenylethane. Sorry about that. Everyone got full credit (4 points) for this problem.

2. **Mechanism.**

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



Perhaps question #24 was helpful here.

3. **Roadmap.** It's roadmap time! You are given some data about five compounds, A-E. Draw the structural formulas of A-E in the boxes provided. Compound A ($C_{26}H_{20}$) undergoes ozonolysis to give only benzophenone, and it reacts with hydrogen (platinum catalyst) to give compound B ($C_{26}H_{22}$). Compound B reacts with hydrogen (rhodium catalyst) to give compound C ($C_{26}H_{46}$). Compound A reacts with bromine to give D ($C_{26}H_{20}Br_2$). D reacts with a mixture of nitric and sulfuric acids to give mostly E ($C_{26}H_{20}Br_2(NO_2)_4$).

