

Answer Key

Department of Chemistry
SUNY/Oneonta

Chem 322 - Organic Chemistry II
Examination #1 - February 12, 2001

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.

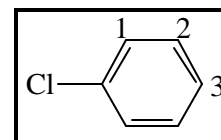
On the Test Scoring Answer Sheet, using a soft pencil, enter the following data (in the appropriate places): your name, instructor's name, your student (Social Security) number, course number (30032201) and the test number (01); darken the appropriate bubbles under the entries, making dark black marks 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 points each.

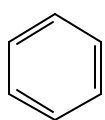
You have 90 minutes. Good luck!

1. Methylbenzene is also known as
(a) phenol. (b) xylene. (c) naphthalene. (d) anthracene. (e) toluene.
2. Hydroxybenzene, Ph-OH, is also known as
(a) phenol. (b) xylene. (c) naphthalene. (d) anthracene. (e) toluene.
3. Consider chlorobenzene shown to the right. The ring positions 1, 2, 3 are called, respectively
(a) meta, ortho, para. (b) ortho, meta, para. (c) para, meta, ortho.
(d) ortho, para, meta. (e) para, ortho, meta,. (f) meta, para, ortho.

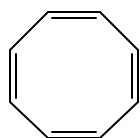


chlorobenzene

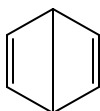
4. Which of the following formulas can be used to calculate the number of π -electrons that would be found delocalized in conjugated monocyclic rings that are aromatic?
[$n = 0, 1, 2, 3, \dots$]
(a) $2n$, (b) $2n+2$, (c) $2n+4$, (d) $4n+2$, (e) $6n$
5. Which of the following skeletal structures is an *accurate and complete* representation of benzene?



(a)



(b)



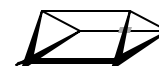
(c)



(d)

(e) None of the above structures accurately represents benzene.

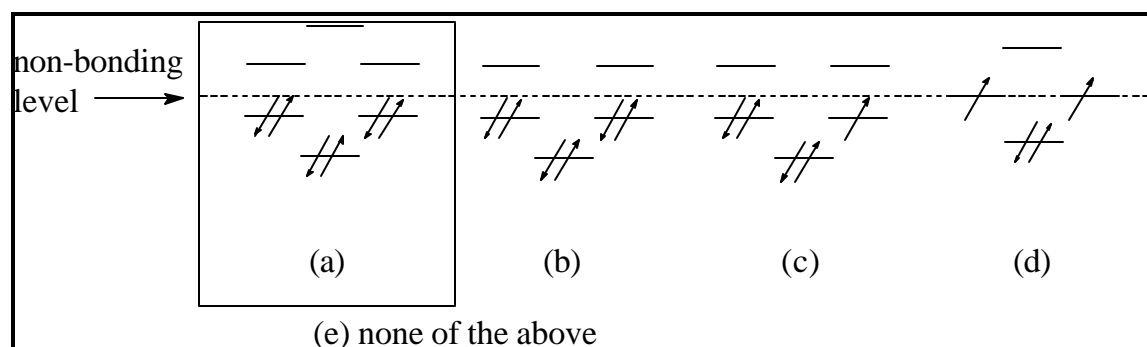
6. The compound shown to the right is known as prismane or Ladenburg benzene. What relationship does this compound bear to benzene?
(a) It is a (poor) resonance structure of benzene.
(b) It is an enantiomer of benzene.
(c) It is a diastereomer of benzene.
(d) It is a constitutional (structural) isomer of benzene.
(e) It bears no relationship to benzene.



7. Which of the following characteristics is *not* associated with aromaticity?

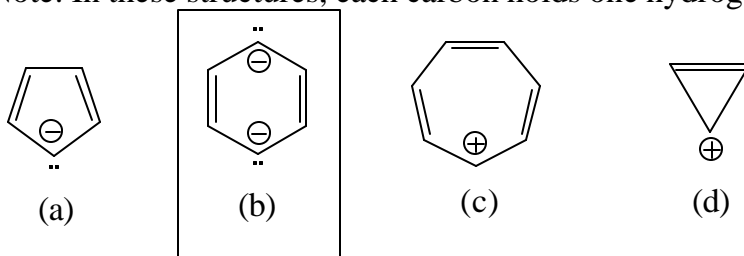
- (a) downfield shift of protons in the NMR spectrum owing to a "ring current",
- (b) ring undergoes electrophilic addition,
- (c) ring undergoes electrophilic substitution,
- (d) there are no sp^3 hybridized atoms in the ring,
- (e) stability

8. Which of the following is a representation of the energy levels and electron occupancy of π molecular orbitals in benzene? Energy increases in the upward direction in the diagram, so bonding orbitals are below the non-bonding level and anti-bonding orbitals are above the non-bonding level.

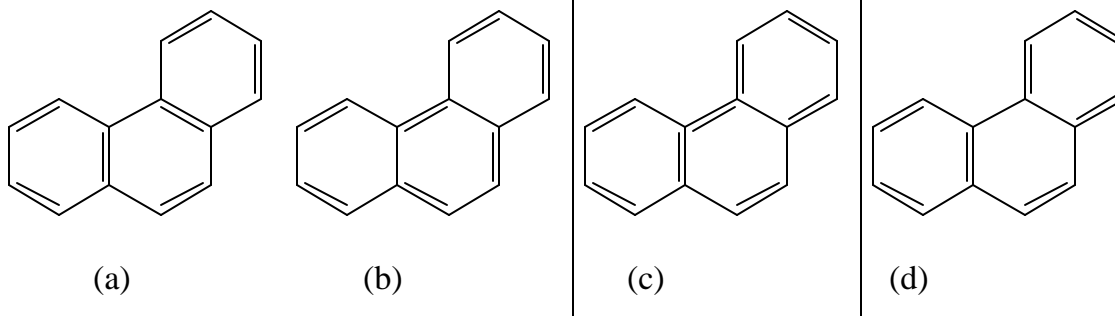


9. According to simple Huckel theory, which of the following rings should *not* be aromatic?

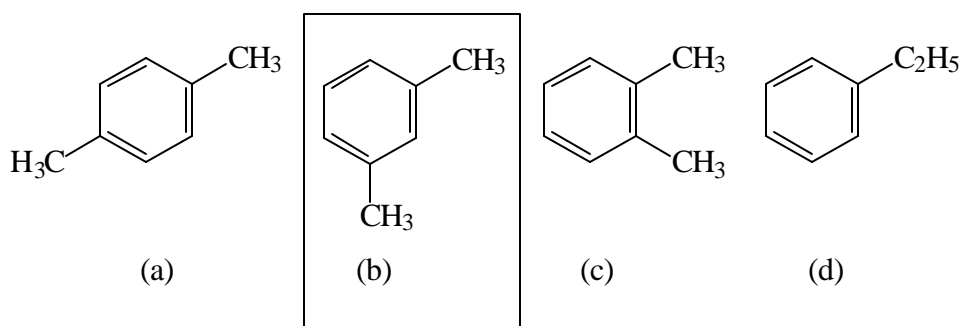
Note: In these structures, each carbon holds one hydrogen.



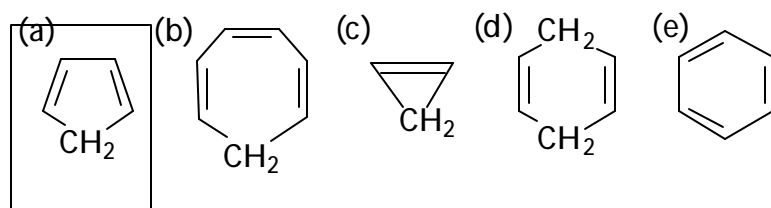
10. Which of the following is *not* a valid resonance structure for phenanthrene?



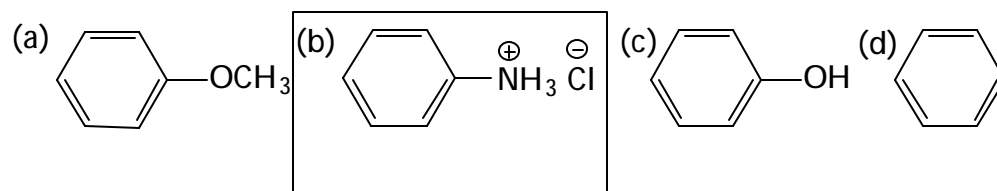
11. Compound A, C_8H_{10} , yields three monobromo substitution products (one major, two minor), C_8H_9Br , on reaction with bromine in the presence of iron. The proton NMR spectrum of A shows a complex multiplet at $\delta = 7.0\text{ppm}$ and a singlet at $\delta = 2.3\text{ppm}$. Which of the following is the structure of A?



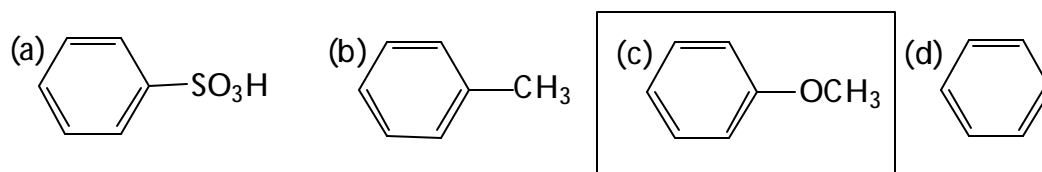
12. Which of the following compounds would most readily lose a proton (H^+) to give a carbanion on treatment with $NaNH_2$ (ie which is most acidic)?



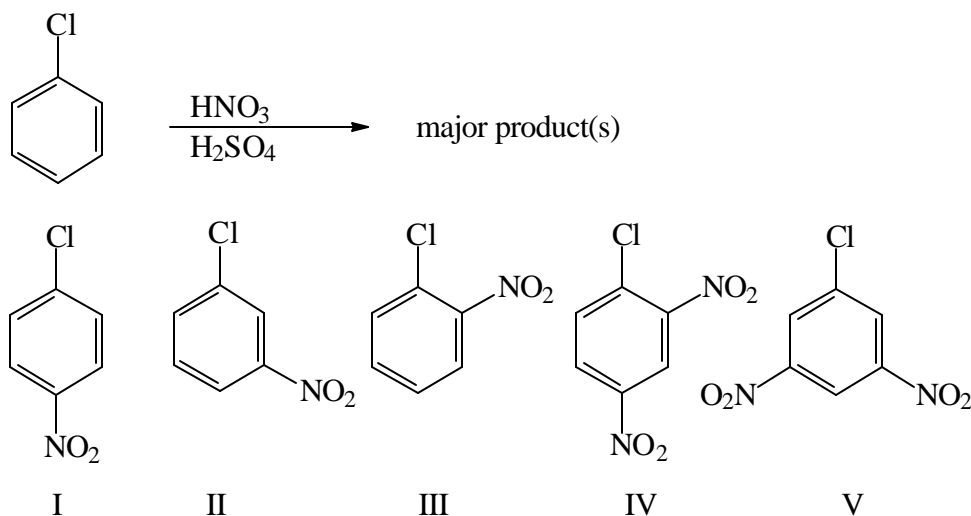
13. Which of the following compounds reacts most slowly with HNO_3/H_2SO_4 ?



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

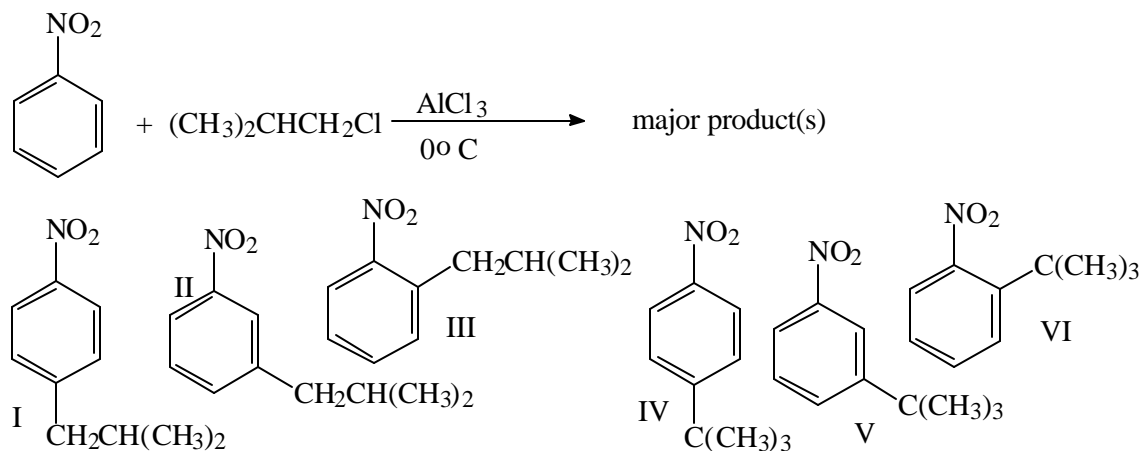


15. Chlorobenzene is reacted with an equimolar amount of nitric acid in the presence of sulfuric acid. What is(are) the major product(s)?



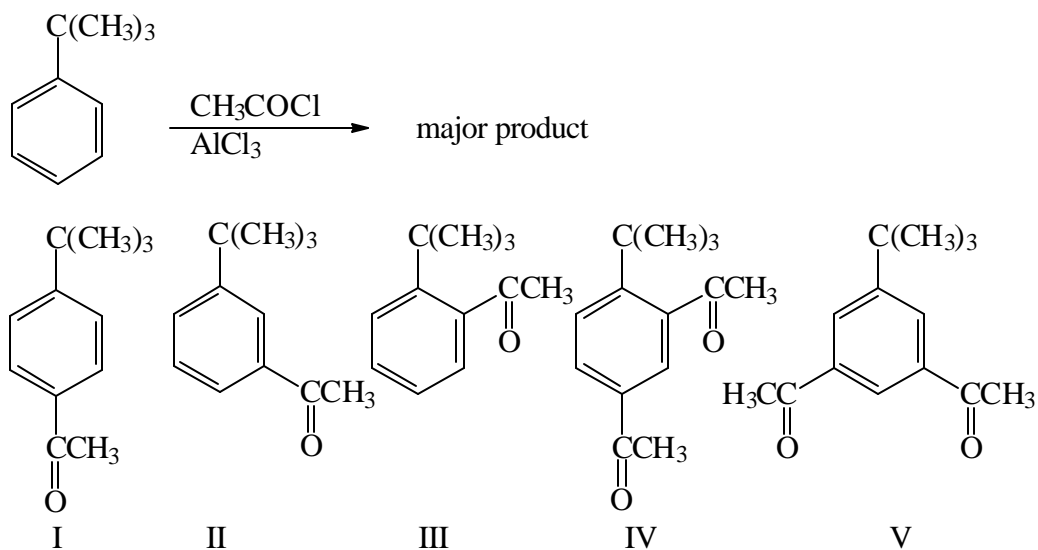
(a) I, (b) II, (c) III, (d) IV, (e) V, (f) I, III, (g) no reaction takes place

16.



(a) I, III (b) II, (c) IV, VI, (d) V, (e) I, III, IV, VI, (f) II, V, (g) No reaction takes place.

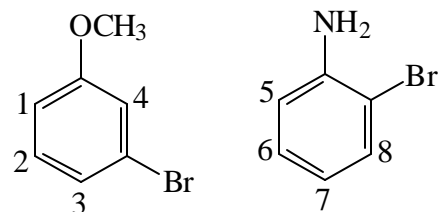
17.



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

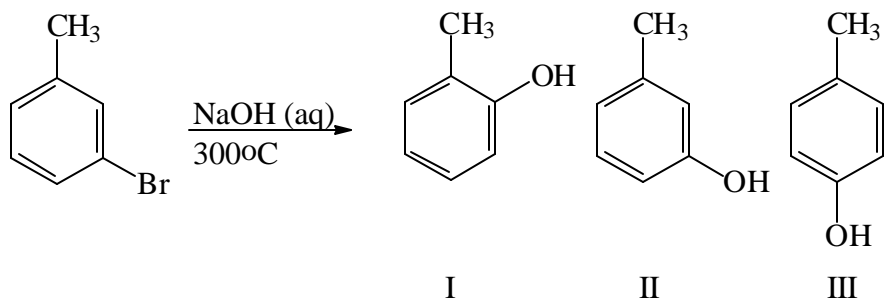
18. Which positions in these molecules would be good sites for electrophilic substitution?

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



19. 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.



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

- (I) 1) Br₂/Fe, 2) HCOOH/KOH.
(II) 1) Br₂/Fe, 2) CH₃Br/AlCl₃, 3) KMnO₄/heat.
(III) 1) HCOOH/KOH, 2) Br₂/Fe.
(IV) 1) CH₃Br/AlCl₃, 2) Br₂/Fe, 3) KMnO₄/heat.
(V) 1) CH₃Br/AlCl₃, 2) KMnO₄/heat, 3) Br₂/Fe.

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

21. Rank the following compounds in order of decreasing reactivity toward *electrophilic* substitution (most reactive first):

- (I) chlorobenzene, (II) 4-nitrochlorobenzene, (III) 2,4-dinitrochlorobenzene,
(IV) 2,4,6-trinitrochlorobenzene.

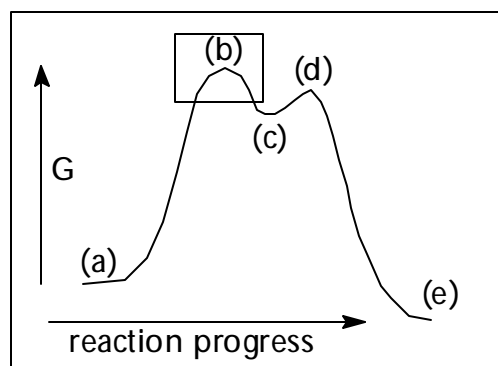
(a) I > II > III > IV, (b) I > III > II > IV, (c) III > I > IV > II, (d) IV > III > II > I,
(e) none of the above answers

22. Rank the following compounds in order of decreasing reactivity toward *nucleophilic* substitution (most reactive first):

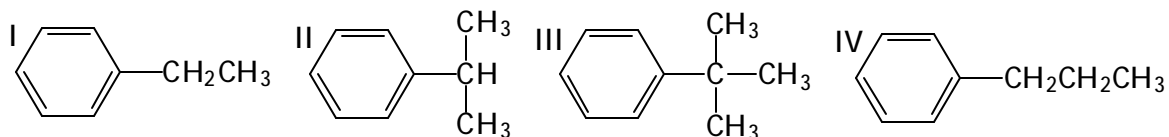
- (I) chlorobenzene, (II) 4-nitrochlorobenzene, (III) 2,4-dinitrochlorobenzene,
(IV) 2,4,6-trinitrochlorobenzene.

(a) I > II > III > IV, (b) I > III > II > IV, (c) III > I > IV > II, (d) IV > III > II > I,
(e) none of the above answers

23. Which point on the reaction diagram to the right represents the transition state for the slow step in the aromatic electrophilic substitution?



24. 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?



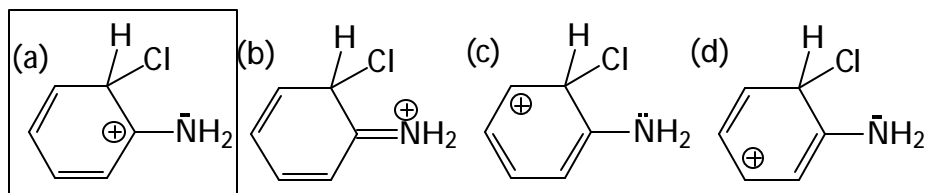
- (a) I, (b) II, (c) III, (d) IV, (e) I&IV, (f) II&III, (g) II-IV
25. Consider the four compounds shown in question #24. Which of these compounds could not be synthesized in good yield by carrying out a Friedel-Crafts *acylation* on benzene, followed by an appropriate reduction?

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

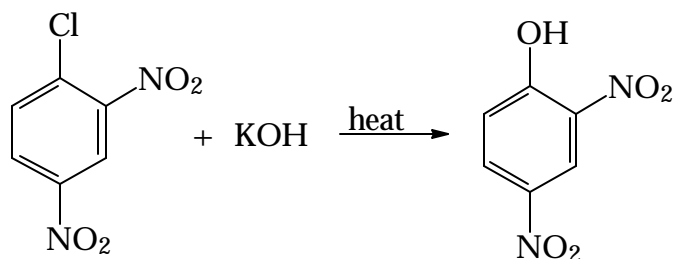
DIRECTIONS: Questions 26-28 are of the type where a statement is followed by an explanation: <Statement> because <Reason>. For each of these questions select the correct response from those immediately following:

- (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.
26. Benzene reacts much more rapidly than cyclohexene with $\text{Br}_2/\text{FeBr}_3$ because benzene has aromatic stabilization. (c)
27. Benzene tends to undergo electrophilic substitution reactions rather than electrophilic addition reactions because electrophilic addition would produce a molecule that no longer has a cyclic conjugated 6π electron aromatic system. (a)
28. FeBr_3 acts as a catalyst in the bromination of benzene because it reacts with bromine to produce something like $\text{FeBr}_4^+\text{Br}^-$. (d)

29. 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 NH_2 group?



30.



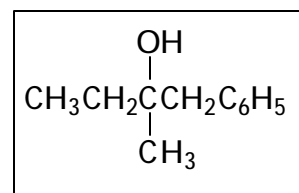
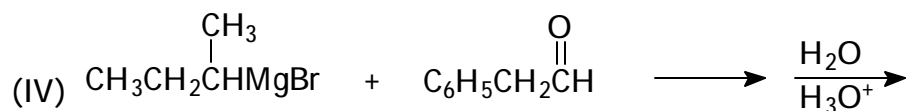
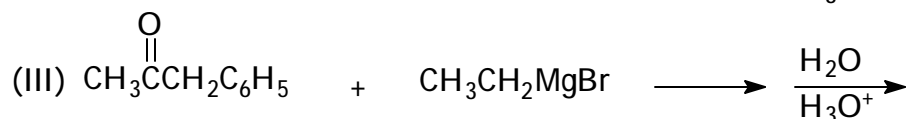
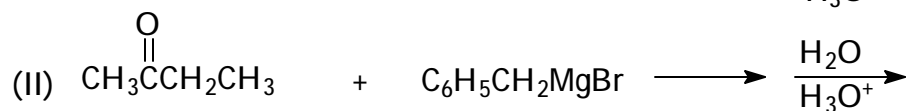
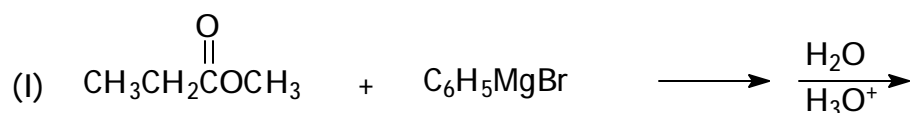
The mechanism for the above reaction involves

- (a) $\text{S}_{\text{N}}1$ substitution of Cl by OH.
 (b) $\text{S}_{\text{N}}2$ 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^- .

31. Which method is most satisfactory for the conversion of 2-butene into 1-butanol?

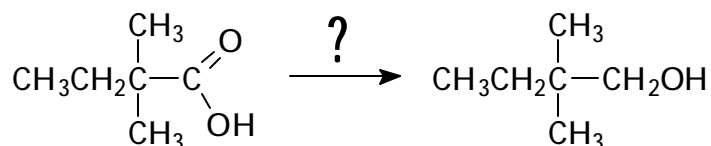
- (a) Reaction with water and sulfuric acid.
 (b) Reaction with water and H_3BO_3 .
 (c) Reaction with B_2H_6 , then reaction with hydrogen peroxide and potassium hydroxide.
(d) Reaction with B_2H_6 , heat the reaction mixture, then reaction with hydrogen peroxide and potassium hydroxide.
 (e) Reaction with $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}$, then NaBH_4 .

32. Which of the following procedures could be used to prepare 1-phenyl-2-methyl-2-butanol?



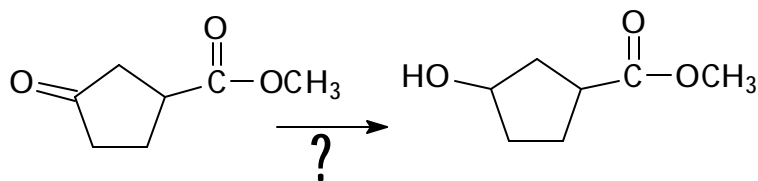
- (a) I&II, (b) II&III, (c) III&IV, (d) I&III, (e) I&IV, (f) II&IV

33. What reagents would you use to bring about the following conversion?

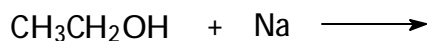


- (a) LiAlH_4 in ether, then $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ (b) CH_3MgBr , then $\text{H}_3\text{O}^+/\text{H}_2\text{O}$
 (c) NaBH_4 , then $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ (d) KMnO_4/KOH , then $\text{H}_3\text{O}^+/\text{H}_2\text{O}$
 (e) Na , $\text{C}_2\text{H}_5\text{OH}$

34. What reagents would you use to bring about the reaction to the right?



- (a) LiAlH_4 , then $\text{H}_2\text{O}/\text{H}_3\text{O}^+$,
 (b) NaBH_4 , then $\text{H}_2\text{O}/\text{H}_3\text{O}^+$,
 (c) NaH , then $\text{H}_2\text{O}/\text{H}_3\text{O}^+$,
 (d) PCC , then $\text{H}_2\text{O}/\text{H}_3\text{O}^+$,
 (e) LiAlH_4 , then PCC
35. Select the major product(s) of the following reaction.



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

36. Which product would be formed, after work up with dilute sulfuric acid, when an excess of phenylmagnesium bromide, Ph-Mg-Br , reacts with methyl benzoate, PhCOOCH_3 ?

- (a) $\text{Ph}_3\text{C-OH}$, (b) $\text{Ph}_2\text{CH-OH}$, (c) Ph-CO-Ph , (d) Ph_3CH ,
 (e) Bogus query! Phenylmagnesium does not react with esters.

37. Which of the following procedures could be used to prepare a primary (1°) 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, IV, (b) II, IV, V, VI, (c) II, V, (d) I, IV, V,
 (e) None of the above answers is correct.

38. 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: $-\text{COOH}$, II: $-\text{COCH}_3$, III: $-\text{NO}_2$

(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.

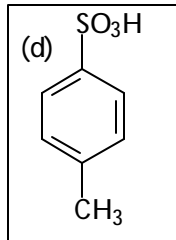
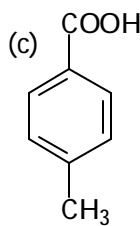
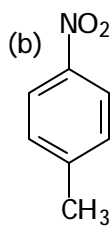
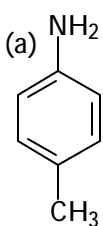
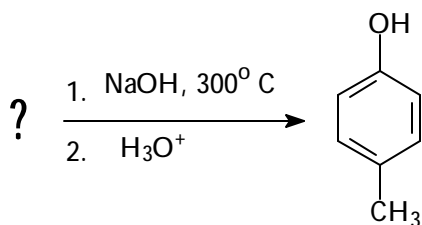
39. Which of the following reagents would be most successful at converting 1-pentanol to pentanal, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{O}$?

(a) KMnO_4 , (b) $\text{CrO}_3/\text{H}_2\text{SO}_4$, (c) $\text{Na}_2\text{CrO}_4/\text{H}_2\text{SO}_4$, (d) $\text{C}_5\text{H}_6\text{NCrO}_3\text{Cl}$ (PCC)/ CH_2Cl_2

40. Which of the following alcohols would undergo acid catalyzed dehydration to give an alkene most easily?

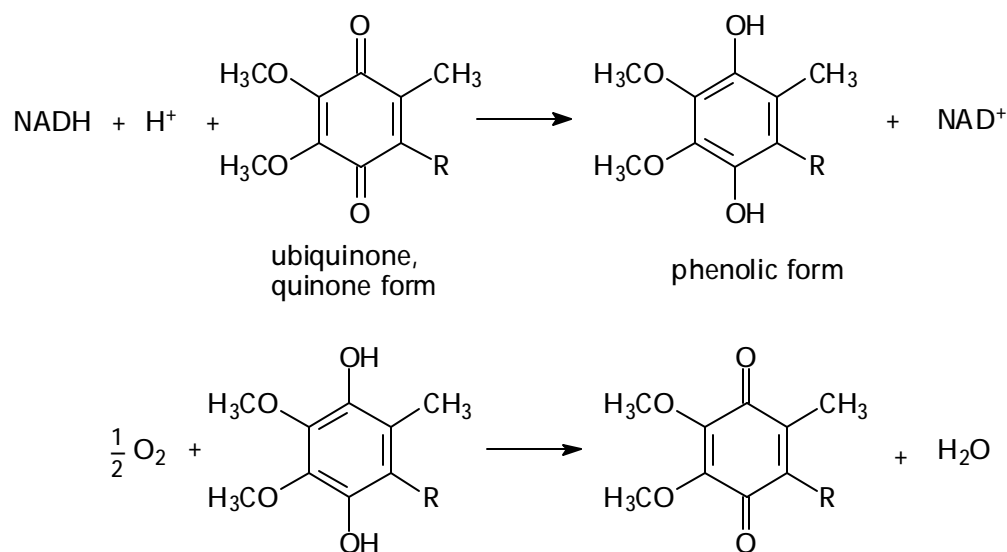
(a) methanol, (b) ethanol, (c) 2-propanol (isopropyl alcohol),
(d) 2-methyl-2-propanol (*t*-butyl alcohol)

41. Which starting material would be appropriate for synthesizing *p*-methylphenol?



42. Ubiquinones function within the mitochondria of cells to mediate the respiration process in which electrons are transported from the biological agent NADH to molecular oxygen. Although a complex series of steps is involved in the overall process, the ultimate result is a cycle whereby NADH is converted to NAD^+ , oxygen is converted to water, and energy is produced.

What are the chemical functions of the quinone and phenolic forms of the ubiquinones?

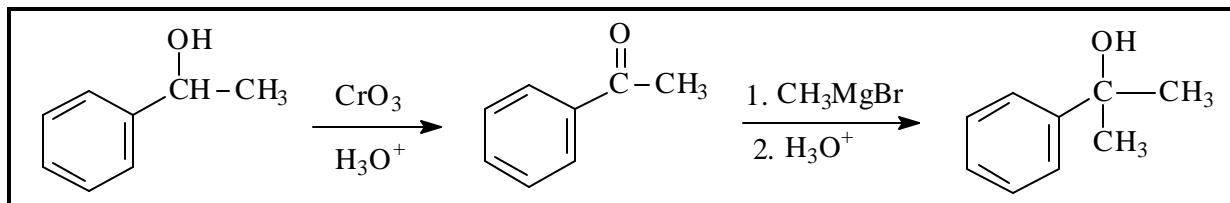


- (a) The quinone form is an oxidizing agent and the phenol form is a reducing agent.
 (b) The phenol form is an oxidizing agent and the quinone form is a reducing agent.
 (c) Both forms are oxidizing agents.
 (d) Both forms are reducing agents.
 (e) None of the above answers is correct.

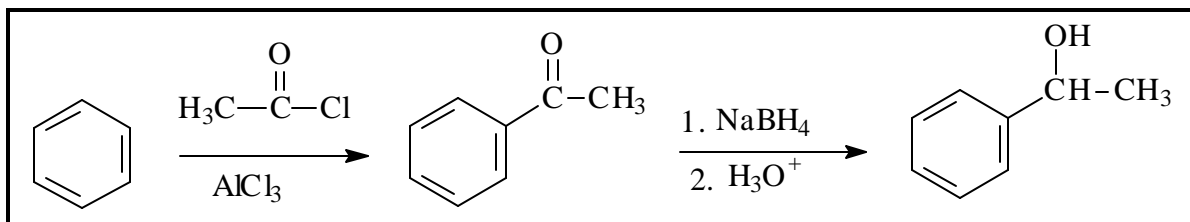
Part II. Enter your answers in the space provided. If there is inadequate room, continue on the back of the page and clearly indicate on the front of the page that you have done this. Hand in this entire exam booklet when you are finished; it will be returned to you with your grade. Make sure your name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

1. **Synthesis.** Draw an outline for each of the following syntheses. More than one step may be required. 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 1-phenylethanol, and using any other materials you need, synthesize 2-phenyl-2-propanol.

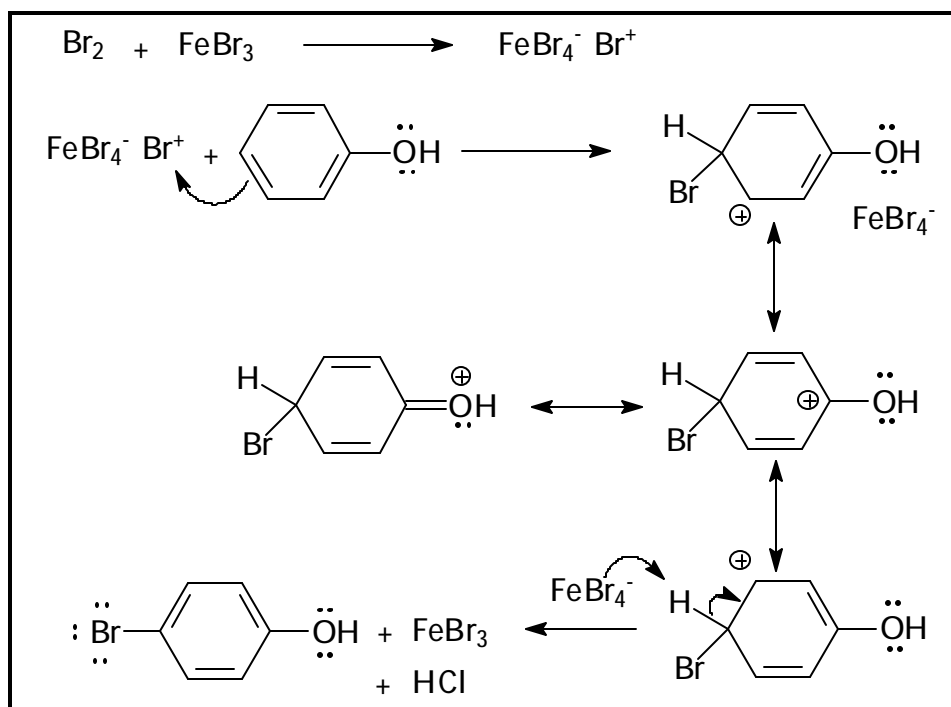
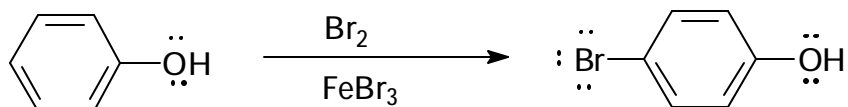


(b) Starting with benzene, and using any other materials you need, synthesize 1-phenylethanol.



2. **Mechanism.**

- (a) 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.



(b) Testosterone is one of the most important male steroid hormones. When testosterone is dehydrated by treatment with acid (Ouch!), rearrangement occurs to yield the product shown. Propose a mechanism to account for this reaction. Show intermediates, not transition states.

