Name_____

Department of Chemistry
SUNY/Oneonta

Chem 322 - Organic Chemistry II
Examination #1 - February 20, 1995

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 entire 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. Which statement best describes the term "aromatic" as used in chemistry?

(a) Aromatic compounds are those that smell. (b) Aromatic compounds are those that smell good. (c) Aromatic compounds are those that smell bad. (d) All compounds that are cyclic are aromatic compounds. (e) Aromatic compounds have highly conjugated rings and are especially stable.

2. Which of the following series of numbers represents the number of 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, ...

3. How many electrons would be found in a bonding π-orbital of an aromatic system?

(a) 0, (b) 1, (c) 2, (d) 6, (e) 0 or 2, (f) 2 or 4 or 6 or 8, *etc*.,
(g) 4 or 8 or 12 or 16, *etc*., (h) 2 or 6 or 10 or 14, *etc*.,

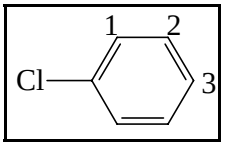
4. Dimethylbenzene is also known as

(a) phenol. (b) xylene. (c) naphthalene. (d) anthracene. (e) toluene.

5. Hydroxybenzene, Ph-OH, is also known as

(a) phenol. (b) phenyl. (c) naphthalene. (d) anthracene. (e) toluene.

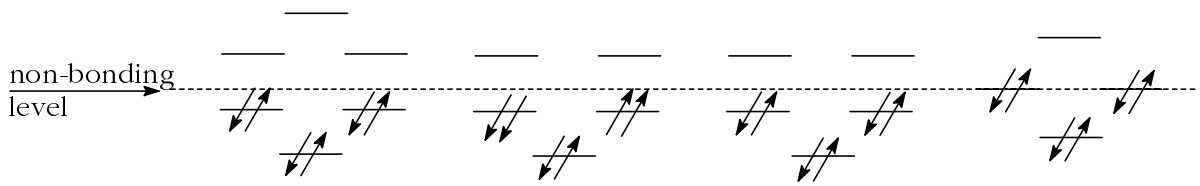
6. Consider chlorobenzene shown to the right. The ring positions labeled 1, 2, 3 are called, respectively



chlorobenzene

(a) meta, ortho, para. (b) ortho, meta, para. (c) para, meta, ortho.
(d) ortho, para, meta. (e) para, ortho, meta,. (f) meta, para, ortho.

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

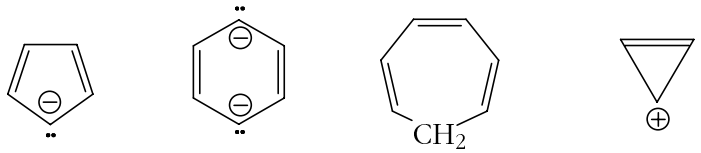


(a) (b) (c) (d)

(e) none of the above

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

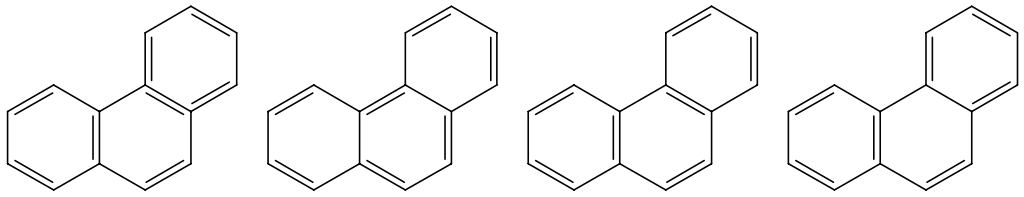
Note: In these structures, each carbon holds one hydrogen, unless otherwise shown.



(I) (II) (III) (IV)

(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?



(a) (b) (c) (d)

10. Aromatic compounds are most prone to undergo which of the following?

(a) heterolytic substitution, (b) homolytic substitution,
(c) heterolytic addition, (d) homolytic addition.

11. Which of the following statements about benzene is <u>incorrect</u>?

(a) All twelve atoms lie in the same plane.
(b) All of the carbon atoms are sp hybridized.
(c) Electrophilic substitution is a common reaction type.
(d) The C-C bonds are all the same length.

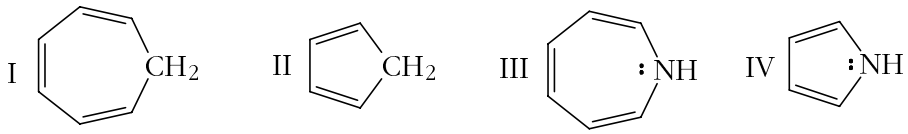
12. Which of the following statements about benzene is <u>incorrect</u>?

(a) It is more reactive than acyclic trienes.
(b) It undergoes addition only with difficulty.
(c) The C-C bond length is shorter than in ethane.
(d) The carbon-hydrogen bond lengths are all the same.

13. How many isomers of nitrodibromobenzene could, in theory, be prepared by the mononitration of *m*-dibromobenzne?

(a) one, (b) two, (c) three, (d) four

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.

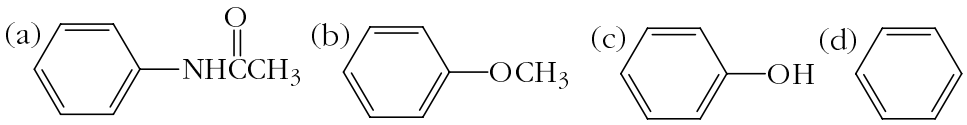
15. Which of the following statements are usually true of aromatic compounds?

I. Electrophilic addition is a common reaction type.
II. Electrophilic substitution is a common reaction type.

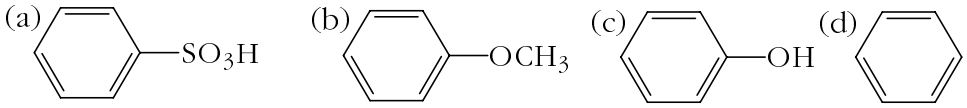
III. Aromatic compounds have relatively large heats of hydrogenation.
IV. Primary hydrogen isotope effects are not usually observed for ring substitution.

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

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

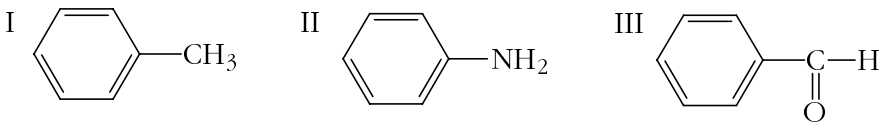


17. Which of the following compounds reacts most rapidly with HNO_3/H_2SO_4?



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

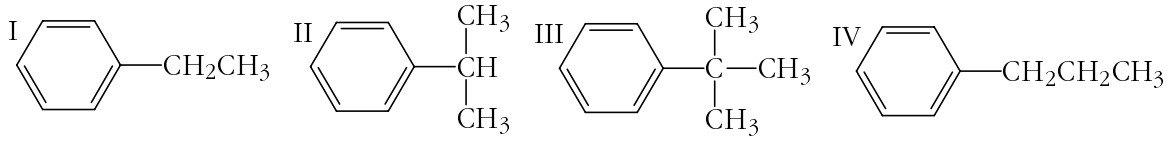
20. Which of the following statements best describes the orientation and reactivity of bromobenzene, C_6H_5-Br, toward electrophilic aromatic substitution?

(a) The entire molecule is deactivated; the meta positions are deactivated the least.
(b) The entire molecule is deactivated; the meta positions are deactivated the most.
(c) The ortho and para positions are activated; the meta postions are deactivated.
(d) The meta positions are activated; the ortho and para positions are deactivated.

21. Which of the following statements best describes the orientation and reactivity of benzoic acid, C_6H_5-COOH, toward electrophilic aromatic substitution?

(a) The entire molecule is deactivated; the meta positions are deactivated the least.
(b) The entire molecule is deactivated; the meta positions are deactivated the most.
(c) The ortho and para positions are activated; the meta postions are deactivated.
(d) The meta positions are activated; the ortho and para positions are deactivated.

22. Consider the four compounds shown above. Which of these compounds could <u>not</u> be



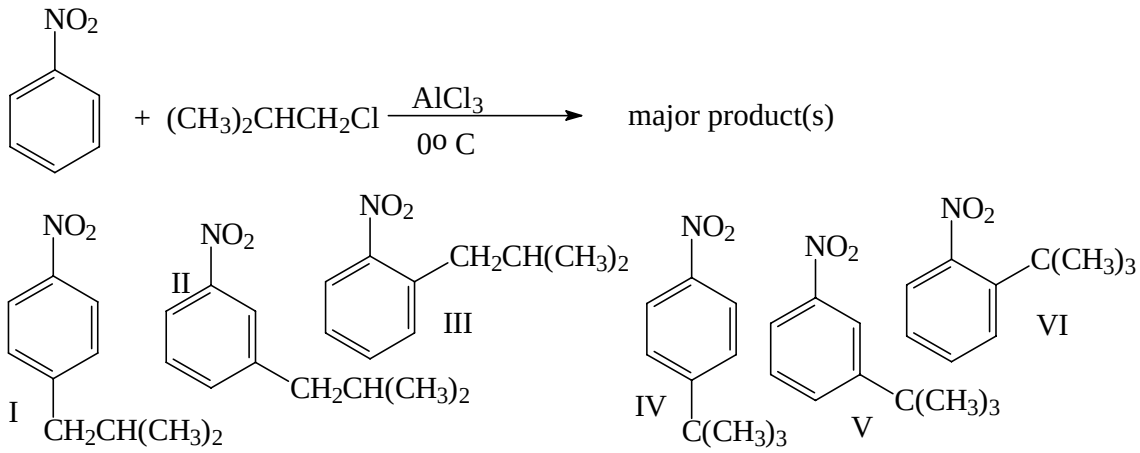
synthesized in good yield by carrying out a Friedel-Crafts *alkylation* on benzene?

(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?

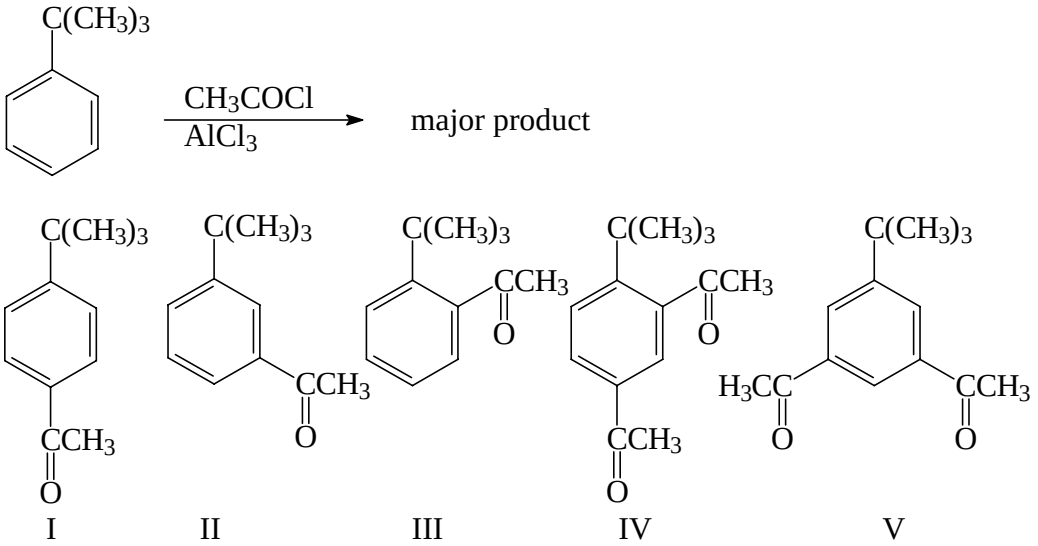
(a) I, (b) II, (c) III, (d) IV, (e) I&IV, (f) II&III, (g) II-IV

24.



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

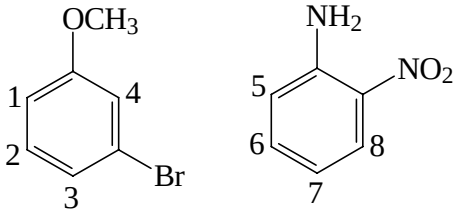
25.



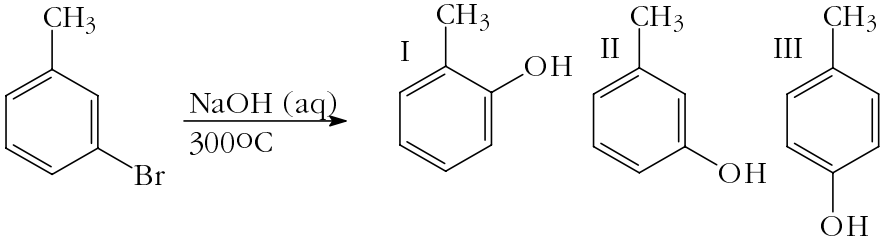
(a) I, (b) II, (c) III, (d) IV, (e) V, (f) no reaction

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

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

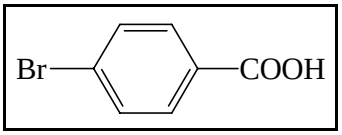


27. Which products would actually form in the reaction shown to the right?



(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*-bromobenzoic acid from benzene?

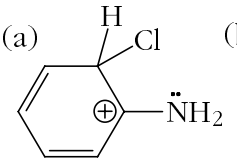
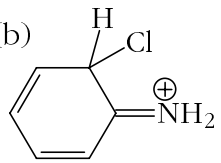
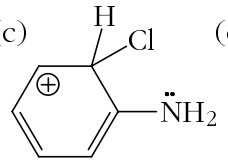
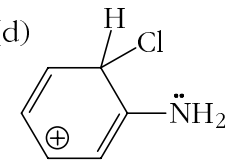


p-bromobenzoic acid

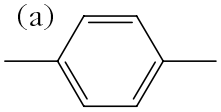
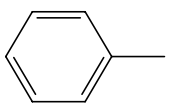
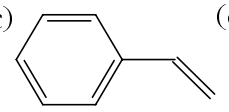
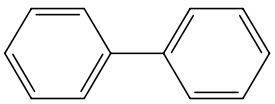
(I) 1) Br_2/Fe, 2) HCOOH/KOH.
(II) 1) Br_2/Fe, 2) $CH_3Br/AlCl_3$, 3) $KMnO_4$/heat.
(III) 1) HCOOH/KOH, 2) Br_2/Fe.
(IV) 1) $CH_3Br/AlCl_3$, 2) Br_2/Fe, 3) $KMnO_4$/heat.
(V) 1) $CH_3Br/AlCl_3$, 2) $KMnO_4$/heat, 3) Br_2/Fe.

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

29. Which of the following resonance structures is <u>least</u> 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?

(a)  (b)  (c)  (d) 

30. Which of the following compounds is styrene?

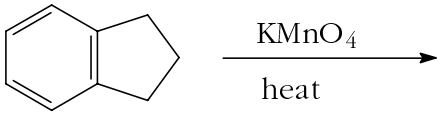
(a)  (b)  (c)  (d) 

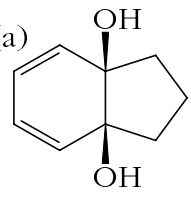
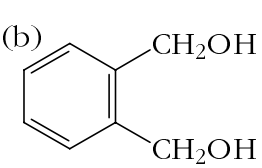
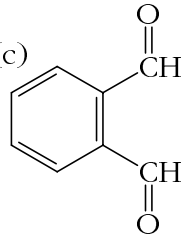
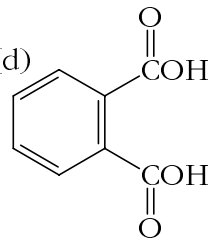
31. With regard to Friedel-Crafts alkylation, which of the following statements are false?

I: Polysubstitution can result in low yields of a desired monosubstituted compound.
II: Aromatic rings less reactive than that in toluene do not react.
III: Aryl and vinyl halides cannot be used in place of alkyl halides.
IV: Aniline does not undergo alkylation.
V: The *ortho* and *para* xylenes formed in the dimethylation of benzene are the result of thermodynamic control.

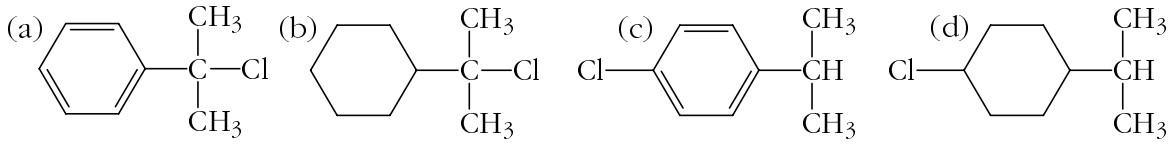
(a) I&II, (b) II&III, (c) III&IV, (d) IV&V, (e) I&IV, (f) II&V, (g) None of the previous answers is correct.

32. What is the major product of the following reaction?

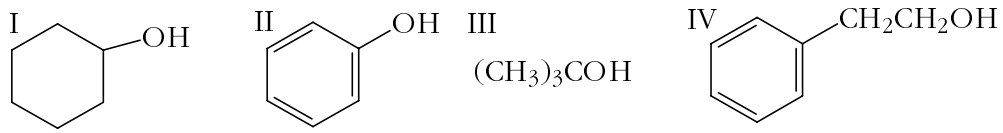


(a)  (b)  (c)  (d) 

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?

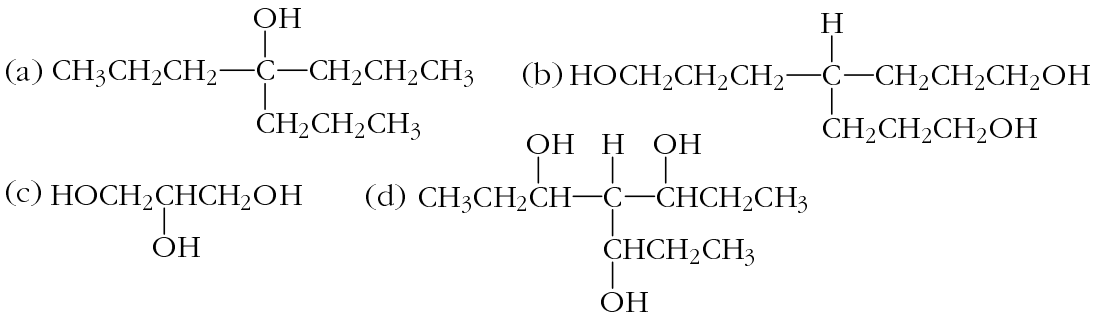


34. Select the answer that correctly identifies the functionality of the following compounds:



	I	II	III	IV
(a)	phenol	phenol	3° alcohol	phenol
(b)	2° alcohol	3° alcohol	1° alcohol	1° alcohol
(c)	2° alcohol	phenol	3° alcohol	1° alcohol
(d)	3° alcohol	phenol	3° alcohol	1° alcohol
(e)	1° alcohol	3° alcohol	2° alcohol	phenol

35. Which of the following compounds is 1,2,3-propanetriol (glycerol)?



36. Alcohols have higher boiling points than alkanes or chloroalkanes of comparable molecular weight. The usual explanation for this is that

(a) hanky panky holds the alcohol molecules together in the condensed (liquid) phase.
(b) hydrogen bonding holds the alcohol molecules together in the condensed phase.
(c) ion-dipole forces hold the alcohol molecules together in the condensed phase.
(d) strong vander Waals forces hold the alcohol molecules together in the condensed phase.

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

I: CH_2CH_2OH, II: H-C≡C-H, III: CH_3CH_3, IV: CH_3COOH, V: C_6H_5-SO_3H

(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.

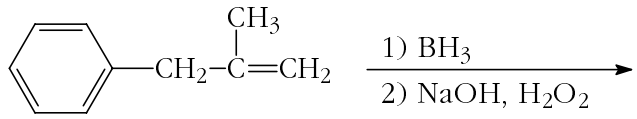
38. Select the major product(s) of the following reaction.

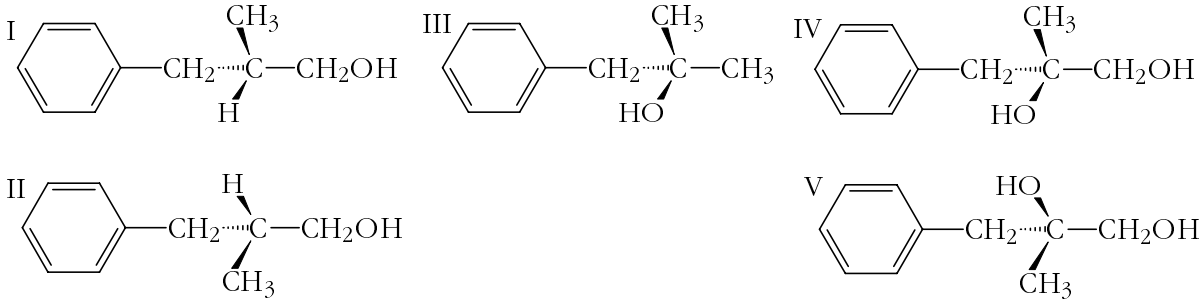
$CH_3CH_2OH + Na \longrightarrow$

(a) $CH_3CH_2O^- Na^+ + H_2$ (b) $CH_3\underset{\underset{O}{\|}}{C}H + NaH$ (c) $Na^+ {}^-CH_2CH_2OH + H_2$

(d) $CH_3CH_2OCH_2CH_3 + NaOH + H_2$ (e) No reaction takes place.

39. Select the principal product(s) of the following reaction.





(a) I, (b) II, (c) I&II in unequal amount, (d) I&II in equal amount (racemic),
(e) III, (f) IV, (g) V, (h) I&V in unequal amount, (i) IV&V in equal amount (racemic)

40. Which of the following procedures could be used to prepare a secondary (2^{o}) 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: $-COCH_3$, III: $-NO_2$

(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.

42. If you wished to form a Grignard reagent from a haloalcohol (a molecule containing both a halogen and hydroxy group) you would need to cloak the -OH group, replacing the H with a protecting group. Which of the following would make the most suitable protecting group?

(a) -$Si(CH_3)_3$, (b) -$COCH_3$, (c) -SO_3H, (d) -$CONH_2$

43. Which of the following attempts to synthesize 1-butanol would be doomed to failure?

(a) React 1-bromobutane with KOH.
(b) React 1-butene with "BH_3" and react the product of that reaction with H_2O_2 and KOH.

(c) Reduce butanal, $CH_3CH_2CH_2CHO$, using lithium aluminum hydride.
(d) React 1-butene with $Hg(OAc)_2$ and react the product of that reaction with $NaBH_4$.

In questions 44 -46 select the missing [?] reagent(s) and conditions which would carry out the indicated transformations in good yield.

44. (a) $CrO_3/H_2SO_4/H_2O$ (Jones' reagent), (b) $KMnO_4/H_2O$, (c) $LiAlH_4$, (d) $NaBH_4$, (e) pyridinium chlorochromate (PCC)/CH_2Cl_2

$(CH_3)_2CHCH_2OH \xrightarrow{?} (CH_3)_2CHC(=O)H$

45. (a) $CrO_3/H_2SO_4/H_2O$ (Jones' reagent), (b) O_2, (c) $LiAlH_4$, (d) $NaBH_4$, (e) $POCl_3$/pyridine, 0° C.

$(CH_3)_2CHCH(OH)CH_3 \xrightarrow{?} (CH_3)_2CHC(=O)CH_3$

46. (a) $LiAlH_4$, (b) $CrO_3/H_2SO_4/H_2O$ (Jones' reagent), (c) H_2/Pt, (d) $NaBH_4$

$CH_3CH_2C(=O)OH \xrightarrow[2.\ H_3O^+]{1.\ ?} CH_3CH_2CH_2OH$

47. Predict the product(s) of the following reaction.

$CH_3CH_2CH(OH)CH(CH_3)_2 \xrightarrow[\text{pyridine}]{POCl_3}$

I > II, means more I than II
I > II+III, means more I than the total of II + III

$CH_3CH_2CH(Cl)CH(CH_3)_2$ I

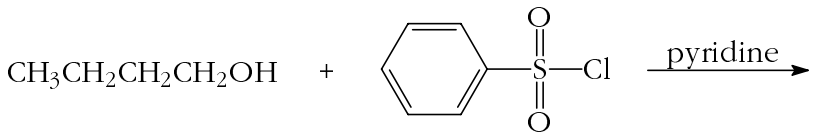
$CH_3CH_2CH{=}C(CH_3)_2$ II

III H_3C, H, H, $CH(CH_3)_2$ (cis)

IV H_3C, H, H, $CH(CH_3)_2$ (trans)

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

48. What is the major product of the following reaction.



(a) CH_2=$CHCH_2CH_3$ (b) CH_3CH═$CHCH_3$

(c) $CH_3(CH_2)_3O$—$SO_2C_6H_5$ (d) $CH_3(CH_2)_3$—$SO_2C_6H_5$

49. Which of the following reagents is frequently used to oxidize primary alcohols to aldehydes?

(a) MnO_2, (b) $KMnO_4$, (c) OsO_4, (d) $C_5H_5NH^+$ CrO_3Cl^-

50. Which of the following reactions is the <u>best</u> method for preparing $(CH_3)_2CHCHClCH_3$?

(a) $(CH_3)_2CHCH_2CH_3$ + $ZnCl_2$, (b) $(CH_3)_2CHCH_2CH_3$ + Cl_2,
(c) $(CH_3)_2CHCHOHCH_3$ + HCl, (d) $(CH_3)_2CHCHOHCH_3$ + PCl_3

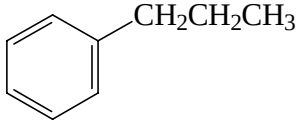
Do Not Detach These Sheets From The Rest Of The Exam

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.

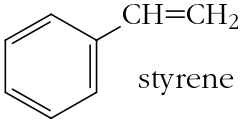
1. Synthesis. Draw an outline for each of the following syntheses. Show all materials and any special conditions employed as you write the reactions which constitute your outline. Do not balance equations or show mechanisms.

(a) Starting with benzene, and using any other materials you need, synthesize propylbenzene in good yield.

propylbenzene



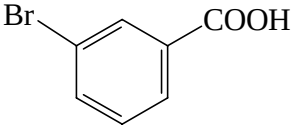
(b) Starting with benzene, and using any other materials you need, synthesize styrene.



styrene

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

m-bromobenzoic acid

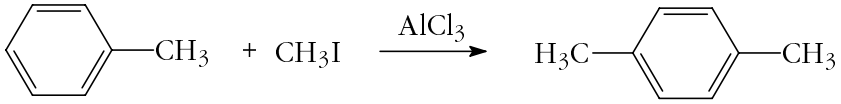


(d) Using organic compounds containing not more than 8 carbons and any other materials you need, synthesize triphenylmethanol, $(C_6H_5)_3C\text{-}OH$.

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

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) 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.