Organic Chemistry II (CHEM 442) MWF 12 Lecture Fall 2015 Dr. Hahn Exam II 10/26/15 M Form A

Sign Name_____Print Name Key

Please show work for all questions for partial and full credit (except multiple choice questions) even on questions which do not specify work. Only answers which are clearly readable will be graded. If you write the answer other than in the intended space without clear indication of where, I will not grade it. (I am grading 250 x 10 page exams. by myself I am not going to spend 3 hours looking for your answer somewhere on the exam and I am not going to contact 250 people to tell me what they meant to write if I can't clearly read what you wrote. No Points for erased answers which are still somewhat visible. No points for errors going from the exam to the scantron. No Points for anything other than normal organic chemistry formulas showing enough information to answer the question. (2 pts print & sign name)

(total number of pages of the exam = 10 pages + periodic table + scantron Check number of pages. If you turn in less than 12 pages, it is your own responsiblity for not completing the exam.)

Part I Multiple Choice (2 pts each, 26 pts total) Fill in your answer on the hardcopy of the exam as backup for your scantron in case you erased so much that there is a computer error in grading.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

1) Which of the following compounds will undergo bromination least rapidly when treated with Br_2 and $FeBr_3$? 1) C

A) acetanilide

B) p-methylacetanilide

C) benzenesulfonic acid

D) benzene

E) bromobenzene

2) Which of the following reagents is the best choice for oxidizing a primary alcohol to an aldehyde? 2) B

A) $LiAlH_4$

B) DMSO, $(COCl)_2$, Et3N (Swern)

C) H_2CrO_4

D) $KMnO_4$

E) $Na_2Cr_2O_7$, H_2SO_4

BA = bad attempt

RRBA = really really bad attempt

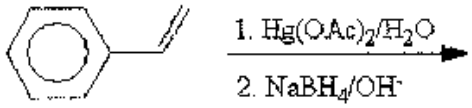
NA = not attempted

NW = no work

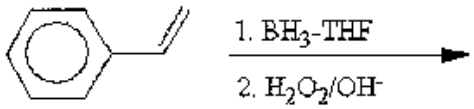
NE = no explanation

3) Which of the following reactions will result in the formation of a secondary alcohol(s) in good yield? 3) E

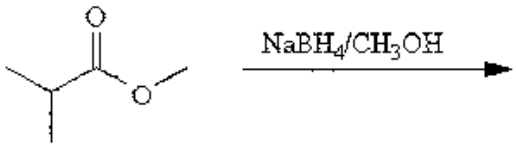
A)



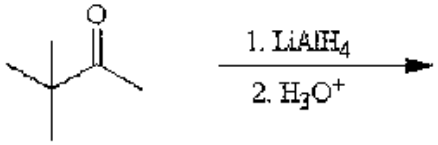
B)



C)



D)



E) both A and D

4) What type of orbital do the lone pair electrons on oxygen occupy in ethanol? 4) A

A) sp^3 B) sp C) π D) p E) σ

5) What compound results when 1-butanol is treated with P/I2? 5) D

A) racemic $CH_3CH_2CHICH_3$

B) $CH_3CH_2CH_2CH_2OP(OH)_2$

C) $CH_3CH_2CH_2CH_2PI_2$

D) $CH_3CH_2CH_2CH_2I$

E) Primary alcohols don't react with P/I2.

6) What descriptive term is applied to the type of diene represented by 1,5-octadiene? 6) A

A) isolated diene

B) alkynyl diene

C) conjugated diene

D) cumulated diene

E) none of the above

7) Which of the following compounds is the most reactive dienophile in a Diels–Alder reaction with 1,3-butadiene? 7) E

A) $CH_2=CH_2$

B) $CH_2=CHOCH_3$

C) $CH_3CH=CHCH_3$

D) $(CH_3)_2C=CH_2$

E) $CH_2=CHCHO$

8) UV spectroscopy measures the energy required to promote an electron from the _____ molecular orbital to the _____ molecular orbital. 8) D

A) lowest occupied, lowest unoccupied

B) lowest occupied, highest unoccupied

C) highest occupied, highest unoccupied

D) highest occupied, lowest unoccupied

E) None of the above

9) Which of the following is also an acceptable name for 3-nitrophenol? 9) B

A) *p*-nitrophenol

B) *m*-nitrophenol

C) *o*-nitrophenol

D) hydroquinone

E) 3-cresol

10) Aromatic molecules contain _____ π electrons. 10) D

A) unpaired

B) no

C) 4n (with n an integer)

D) 4n + 2 (with n an integer)

E) 4n + 1 (with n an integer)

11) In electrophilic aromatic substitution reactions a bromine substituent: 11) B

A) is an activator and an o,p-director.

B) is a deactivator and an o,p-director.

C) is a deactivator and a m-director.

D) is an activator and a m-director.

E) none of the above

12) 2-Methylbutan-1-ol is classified as _____. __. 12) C

A) an enol

B) a secondary alcohol

C) a primary alcohol

D) a phenol

E) a tertiary alcohol

13) What is the major difference between an antiaromatic and aromatic compound? 13) E

A) Aromatic compounds cannot have a charged atom in the structure

B) The structure must be cyclic for aromatic but not antiaromatic compounds?

C) Antiaromatic compounds have at least one *sp*3 hybridized atom in the ring

D) Antiaromatic compounds can assume a chair-like structure while aromatic compounds are nearly flat

E) Only aromatic compounds follow Huckle's rule.

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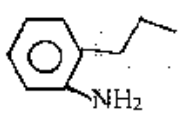
II. Short Answers (39 pts)

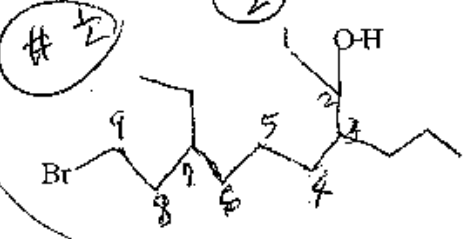
A. Nomenclature: (2 pts each, 8 pts)

1. Given the structural formula shown below, give the IUPAC name of the molecule.

a. name 2-propyl aniline or aniline 2-propyl or propyl aniline

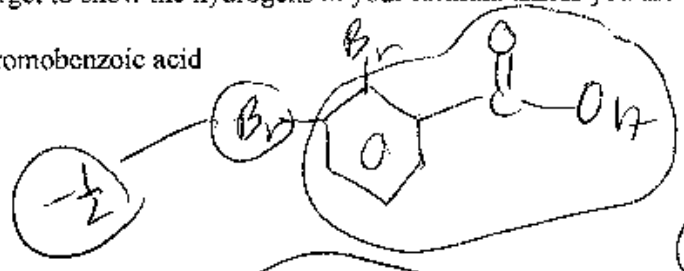


b. name 9-bromo-7-ethyl-3-propyl nonan-2-ol

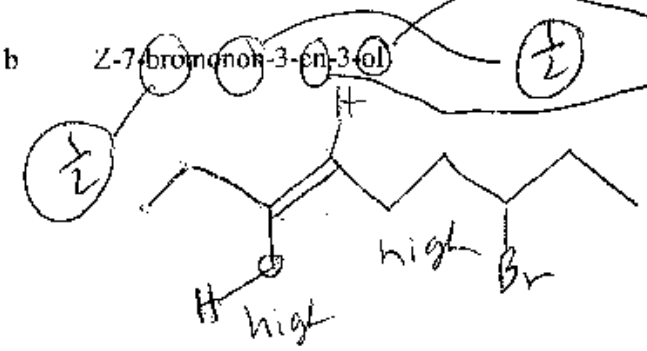


2. Given the following IUPAC name, draw a structural formula of the molecule (skeletal formula acceptable, condensed structure, Lewis Dot structure acceptable, molecular formula not acceptable - don't forget to show the hydrogens in your formula unless you are using the skeletal structure.)

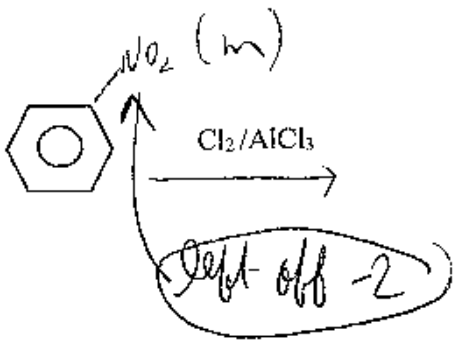
a 2,3-dibromobenzoic acid

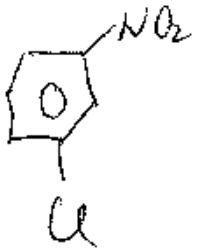


b Z-7-bromonon-3-en-3-ol

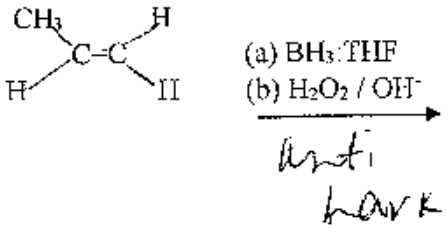


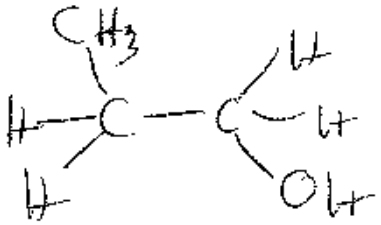
B. Reactions: Show the Organic Product in the following reactions by giving the structural formula of the product. (skeletal formula, condensed structure, Lewis Dot structure are all acceptable. Molecular Formula is **not** acceptable.) DO **NOT** SHOW MECHANISMS. You will only earn points for product which are correct or are regioisomers, or enantiomers of the correct product or is an intermediate on the way to produce the correct product. **I will give no points --zero points for anything else.** (2 pts each, 8 pts)

1) 

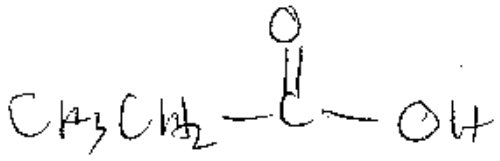


regio -1
stereo -1
intermediate -1
left off -2
oxidized too far
not enough -1

2) 



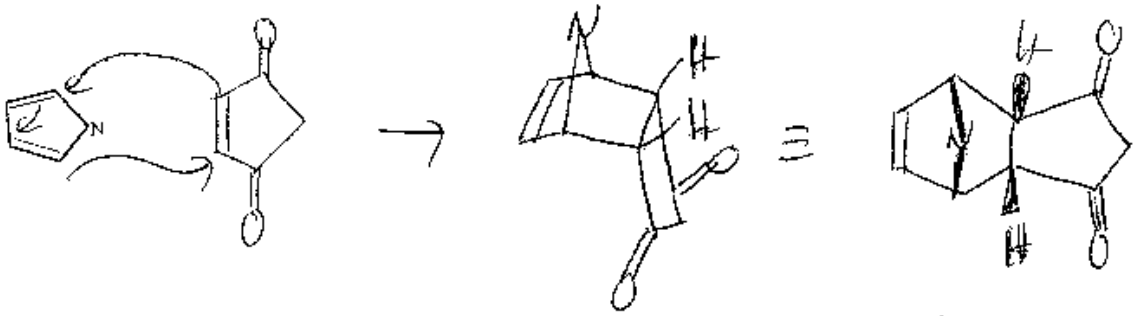
3) CH_3CH_2-O-H $\xrightarrow{PCl_5}$ CH_3CH_2-Cl

4) CH_3-CH_2-CH_2O-H $\xrightarrow{Na_2Cr_2O_7 / H^+}$ 

C. Short Answers part of Short Answers: (23 pts)

1pt did not circled

1. Given the following Diels Alder Reaction, give the correct product. Is the product which you drew (a) cis (trans) product from a cis (trans) dienophile (b) an endo (exo) product (c) not allowed because of the s-trans (s-cis) diene ? Circle one to all of the letters. (5 pts, 1 pt circling)

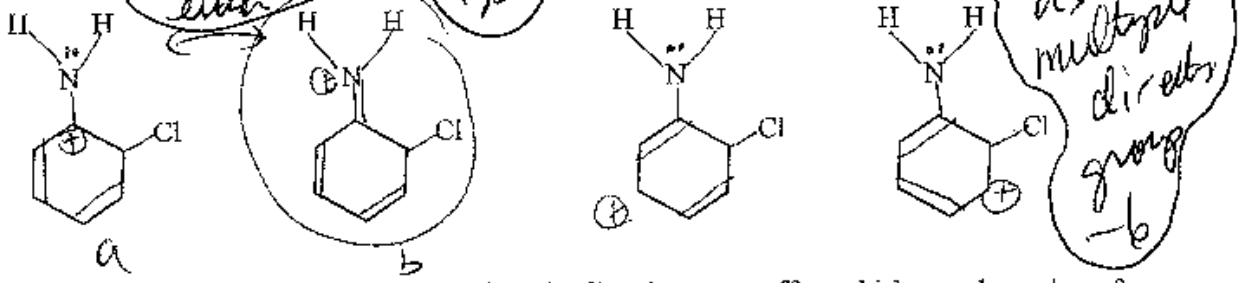


2 a. Given the following resonance structures, does the directing group shown act as a [(o,p activator) or (m deactivator)] (circle one entire parenthesis). (2 pts each, 8 pts total)

2pt

Circled either a or b

4pt



treated as multiple directing group -b

b. Which of the resonance structures determines the directing group effect which you chose above ? Circle the resonance structure and explain. You may circle more than one resonance structure and explain both resonance structures which you chose. (4 pts)

2pts explan

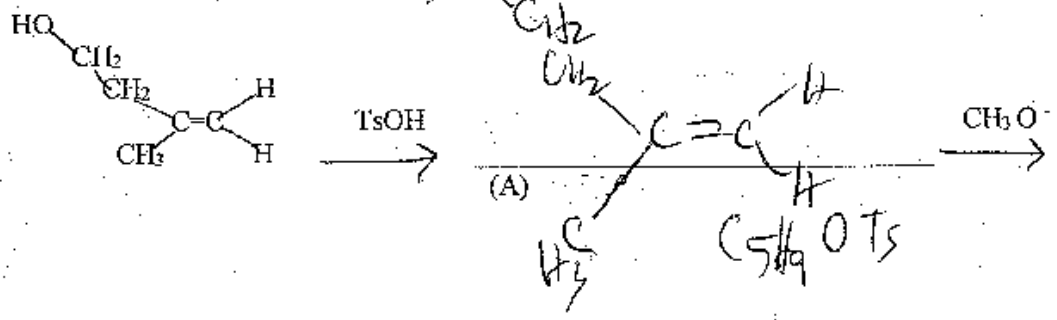
⊕ is an extra resonance structure w ⊕ charge taken outside the arene ring stabilizing ortho. @ also has edg NH_2 next to ⊕ charge. These stabilize ortho (+ similar for para) resulting in o|p product

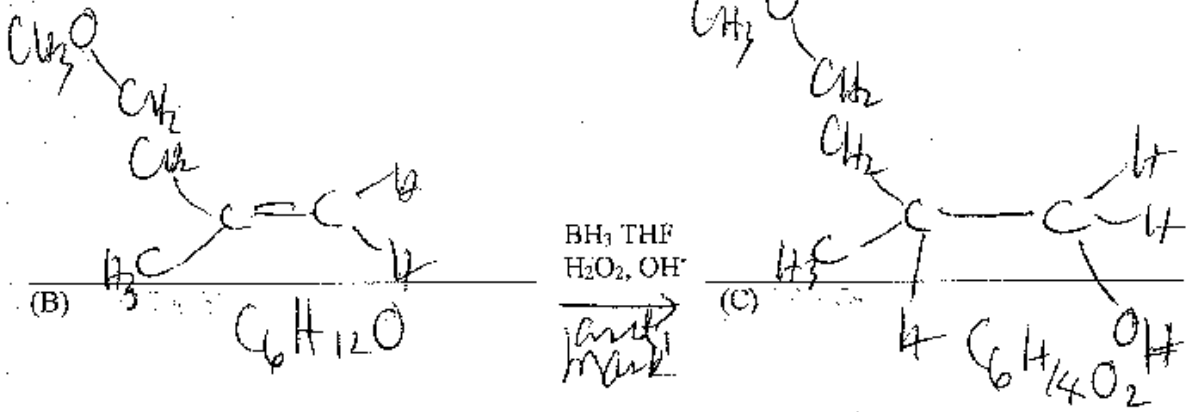
NE -2

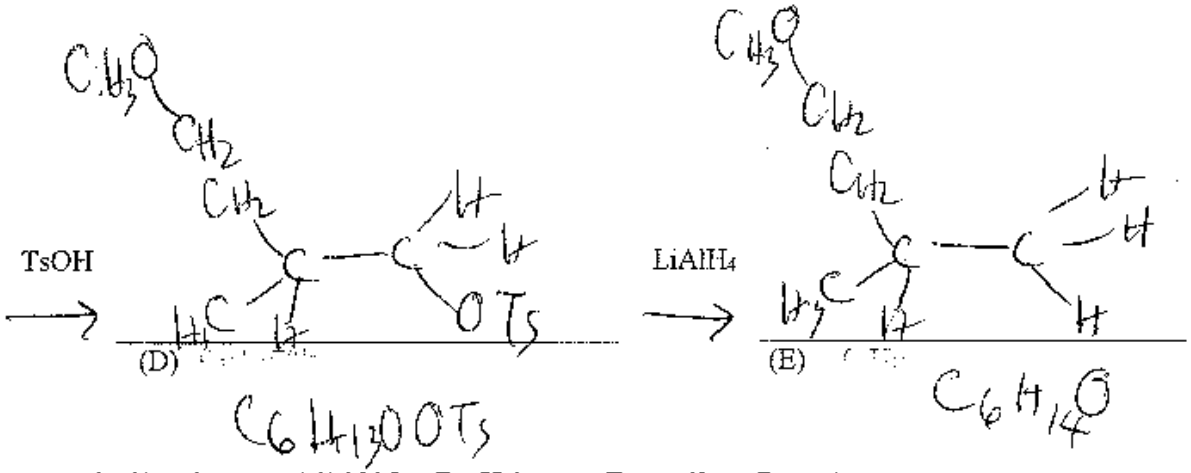
attempt -1

3 Complete the following synthesis by filling in the blank. I have provided some hints to help you come up with the answers. NOTE: The way I grade this is for you to fill in reasonable molecules based on the immediate prior molecule. i.e. If you fill in part A with the wrong molecule and then do the next reaction to molecule B correctly you will get half credit for answering B correctly. If you fill in B with what you would have gotten if you got A correctly but which cannot possibly be generated from your wrong A, you will lose all credit even if it matches what you should have gotten. (There is no way that you can come up with this answer except perhaps by guessing.) (2 pts each, 10 pts total)

NL – not likely –1 50 – sort of OK.

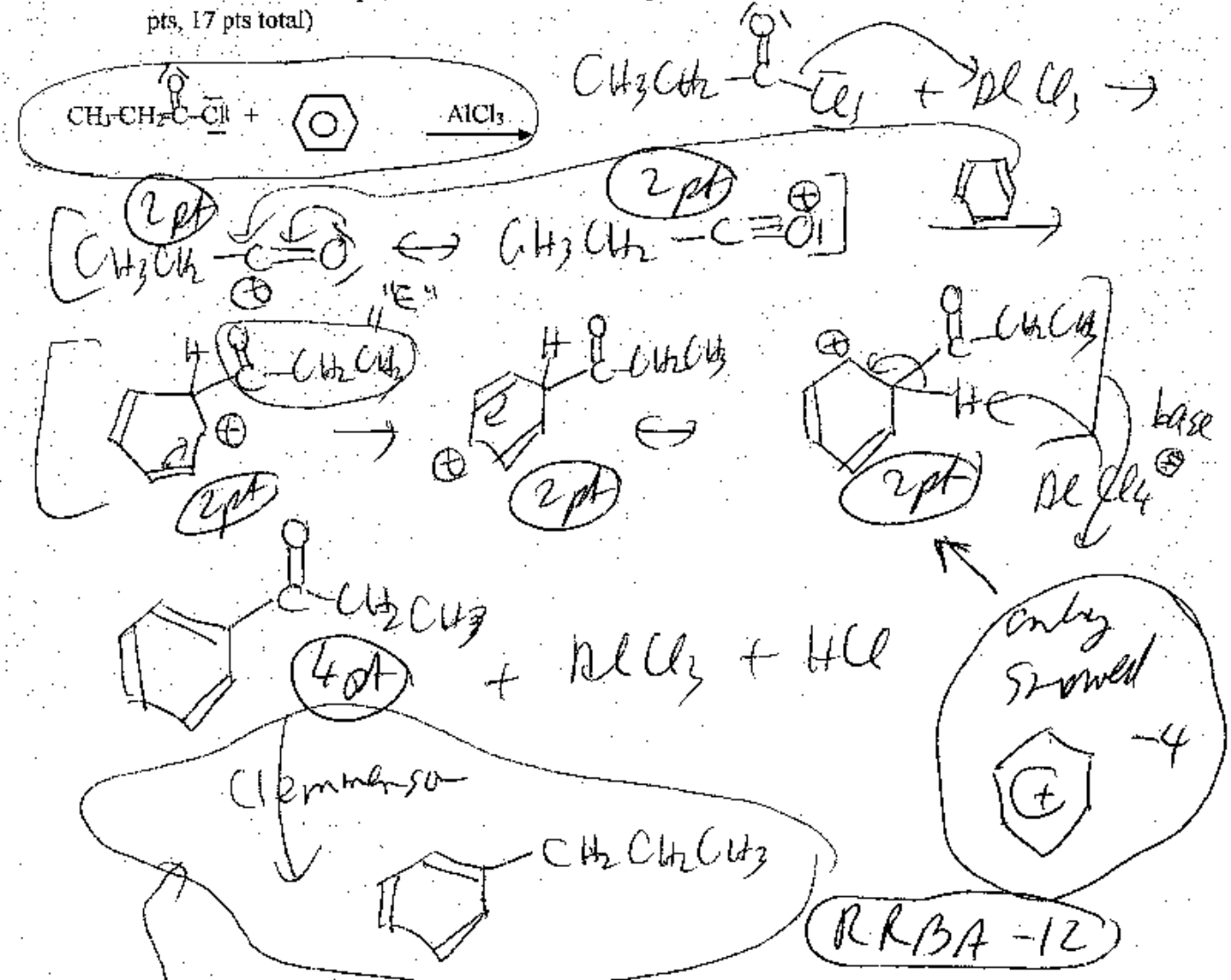






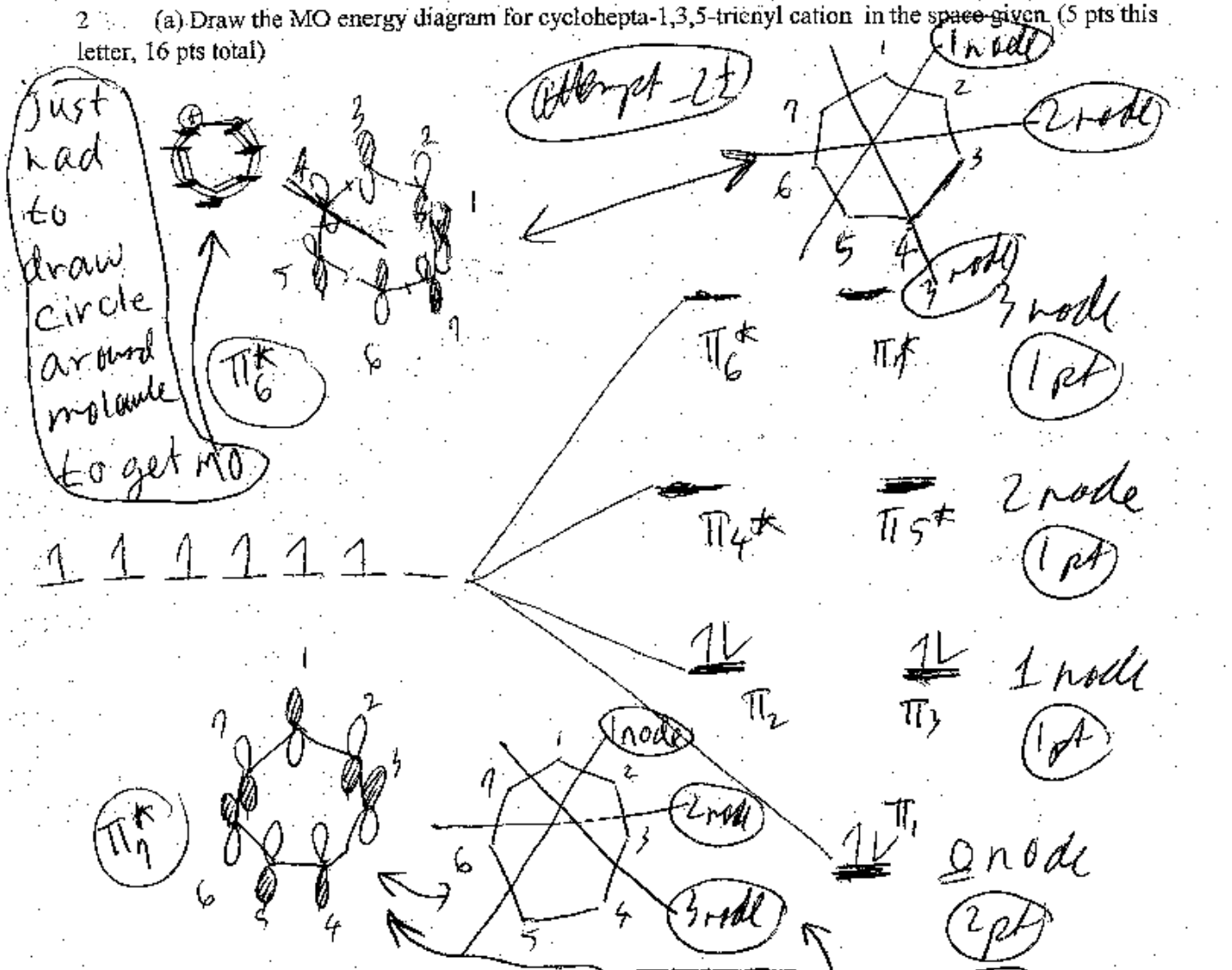
Part III. Long Answers (33 pts) Show work where applicable.

1. a. Show the mechanism of the generation of the electrophile for the following Friedel Craft ~~alkylation~~ (acylation) then show the entire reaction mechanism including the resonance structures of the arenium to the final product. If there is a rearrangement in the mechanism, you should show it. (14 pts, 17 pts total)



b. How would you use the product of the Friedel Craft acylation to attach a primary alkyl to benzene ? Why can't you just attach a primary alkyl group to a benzene using Friedel Craft Alkylation ? Explain. (3 pts) do Clemmensen reduction to get rid of the acyl group. Normally with $CH_3CH_2CH_2-Cl$, a 1° carbocation would rearrange to a 2° carbocation BA -2

2 (a) Draw the MO energy diagram for cyclohepta-1,3,5-trienyl cation in the space given. (5 pts this letter, 16 pts total)



(b) Show the p orbital atomic orbital combination for the highest π^* MO in your energy diagram above in part (a) by the MO which matches. Represent the math sign of your p orbital lobes by shading in one of the lobes in all of the p orbitals. Show the nodes. (3 pts)

either π_6^* or π_7^* attempt -1pt asked for

(c) Fill your MO energy diagram [which you drew above in (a)] with the appropriate number of electrons for the cyclohepta-1,3,5-trienyl cation. Use up and down arrows to represent electrons. (4 pts)

attempt -2pt consistent OK one not 7

(d) Show a Huckel rule explanation of the stability/instability of your cyclohepta-1,3,5-trienyl cation (Huckel Rule is $4n+2 = \#\ \pi$ electrons) (4 pts)

n = 1 $4n+2=6$ $4n=6-2$ $4n=4$ $n=1$ math -1pt

aromatic

Organic Chemistry II (CHEM 442) MWF 12 Lecture Fall 2015 Dr. Hahn Exam II 10/26/15 M Form B

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(B) DMSO, $(COCl)_2$, Et_3N (Swern)

C) H_2CrO_4

D) $KMnO_4$

E) $Na_2Cr_2O_7$, H_2SO_4

(A = bad attempt)

(RRBA - really really bad attempt)

2) Which of the following is also an acceptable name for 3-nitrophenol? 2) B

A) *p*-nitrophenol

(B) *m*-nitrophenol

C) *o*-nitrophenol

D) hydroquinone

E) 3-cresol

(NA = not attempted)

(NW = no work)

(NE = no explanation)

3) What descriptive term is applied to the type of diene represented by 1,5-octadiene? 3) A

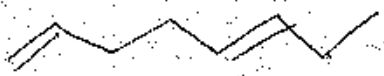
(A) isolated diene

B) alkynyl diene

C) conjugated diene

D) cumulated diene

E) none of the above



4) Aromatic molecules contain _____ π electrons. 4) D

A) unpaired

B) no

C) 4n (with n an integer)

(D) 4n + 2 (with n an integer)

E) 4n + 1 (with n an integer)

5) In electrophilic aromatic substitution reactions a bromine substituent: 5) B

A) is an activator and an o,p-director.

(B) is a deactivator and an o,p-director.

C) is a deactivator and a m-director.

D) is an activator and a m-director.

E) none of the above

6) What type of orbital do the lone pair electrons on oxygen occupy in ethanol? 6) A

(A) sp^3 B) sp C) π D) p E) σ

7) What compound results when 1-butanol is treated with P/I_2? 7) D

A) racemic $CH_3CH_2CHICH_3$

B) $CH_3CH_2CH_2CH_2OP(OH)_2$

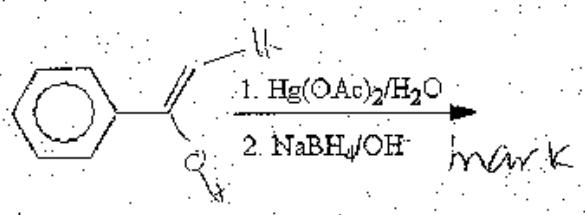
C) $CH_3CH_2CH_2CH_2PI_2$

(D) $CH_3CH_2CH_2CH_2I$

E) Primary alcohols don't react with P/I_2.

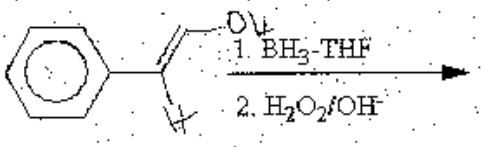
8) Which of the following reactions will result in the formation of a secondary alcohol(s) in good yield? 8) C

A)

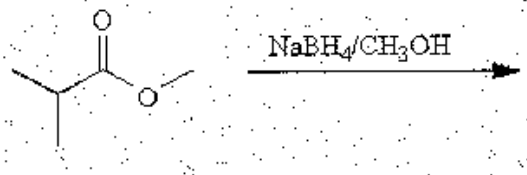


mark

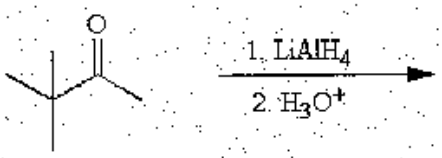
B)



C)



D)



E) both A and D

9) UV spectroscopy measures the energy required to promote an electron from the _____ molecular orbital to the _____ molecular orbital. 9) D

A) lowest occupied, lowest unoccupied

B) lowest occupied, highest unoccupied

C) highest occupied, highest unoccupied

(D) highest occupied, lowest unoccupied

E) None of the above

10) 2-Methylbutan-1-ol is classified as _____. 10) C

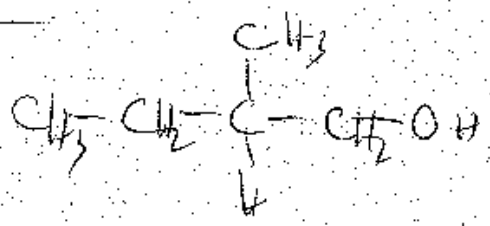
A) an enol

B) a secondary alcohol

(C) a primary alcohol

D) a phenol

E) a tertiary alcohol



11) What is the major difference between an antiaromatic and aromatic compound? 11) E

A) Aromatic compounds cannot have a charged atom in the structure

B) The structure must be cyclic for aromatic but not antiaromatic compounds?

C) Antiaromatic compounds have at least one *sp*3 hybridized atom in the ring

D) Antiaromatic compounds can assume a chair-like structure while aromatic compounds are nearly flat

E) Only aromatic compounds follow Huckle's rule.

12) Which of the following compounds will undergo bromination least rapidly when treated with Br_2 and $FeBr_3$? 12) C

A) acetanilide activator

B) p-methylacetanilide C activator

C) benzenesulfonic acid — m dear

D) benzene — no activation

E) bromobenzene o, p dear

13) Which of the following compounds is the most reactive dienophile in a Diels–Alder reaction with 1,3-butadiene? 13) E

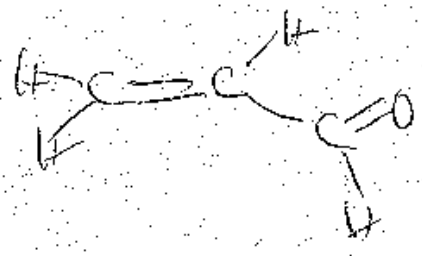
A) $CH_2=CH_2$

B) $CH_2=CHOCH_3$ edg

C) $CH_3CH=CHCH_3$ edg

D) $(CH_3)_2C=CH_2$ edg

E) $CH_2=CHCHO$ ewg



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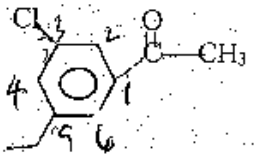
II. Short Answers (39 pts)

A. Nomenclature: (2 pts each, 8 pts)

1. Given the structural formula shown below, give the IUPAC name of the molecule.

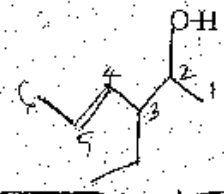
a. name 3-chloro-5-ethylacetophenone



Chlor[illegible] o acetopherone

ethoxe yl (# ½pt) (not alphabetical OK)

b. name (E)-3-ethylhex-4-en-2-ol



hex[illegible] ene 4 ol-2

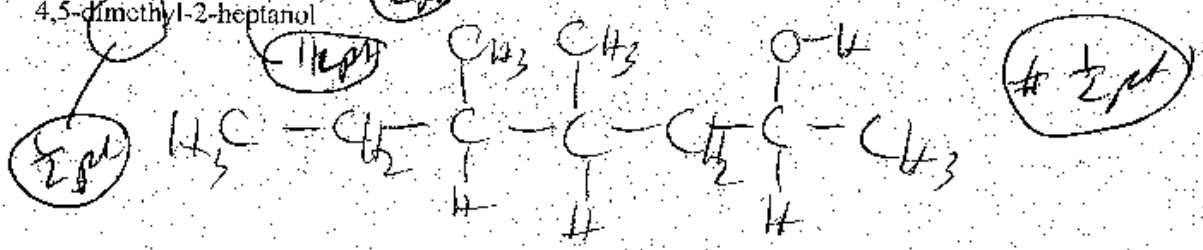
eth[illegible] yl 3 (# ½pt)

spelling - no pt off

2. Given the following IUPAC name, draw a structural formula of the molecule (skeletal formula acceptable, condensed structure, Lewis Dot structure acceptable, molecular formula not acceptable - don't forget to show the hydrogens in your formula unless you are using the skeletal structure.)

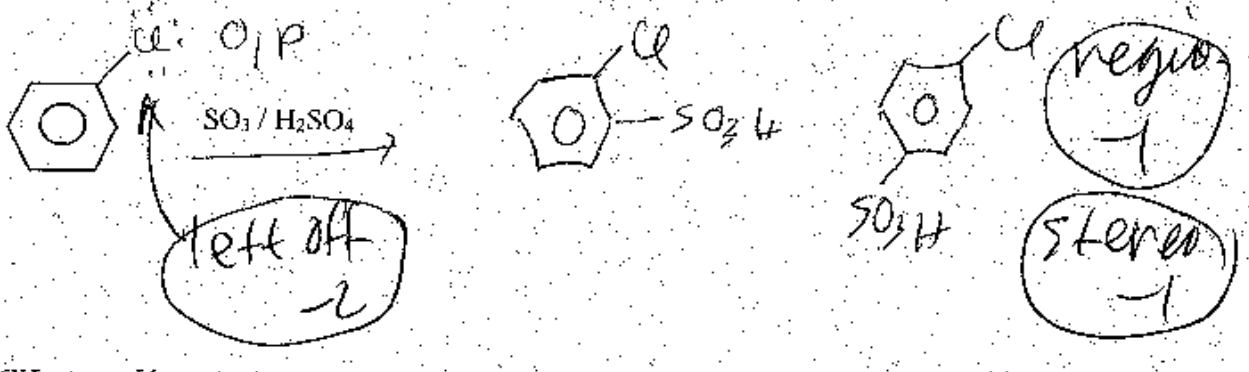
a m-nitroaniline

b 4,5-dimethyl-2-heptanol



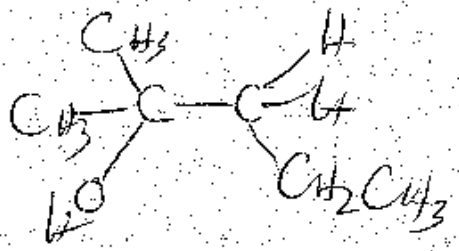
B. Reactions: Show the Organic Product in the following reactions by giving the structural formula of the product. (skeletal formula, condensed structure, Lewis Dot structure are all acceptable. Molecular Formula is **not** acceptable.) DO **NOT** SHOW MECHANISMS. You will only earn points for product which are correct or are regioisomers, or enantiomers of the correct product or is an intermediate on the way to produce the correct product. **I will give no points –zero points for anything else.** (2 pts each, 8 pts)

1)



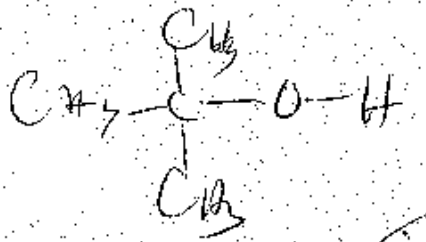
2) CH_3, H, CH_3, CH_2CH_3

(a) $Hg(OAc)_2$, H_2O
(b) OH^-, $NaBH_4$
"mark"



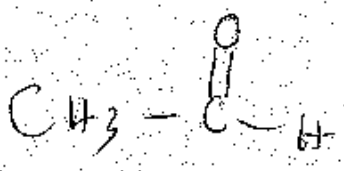
3)

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + H_2O \rightarrow (S_N1)$$



intermediate
-1

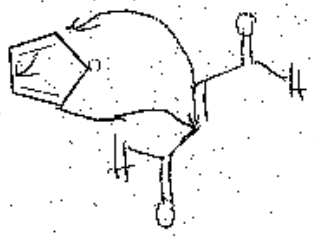
4) CH_3-CH_2-O-H Dess Martin

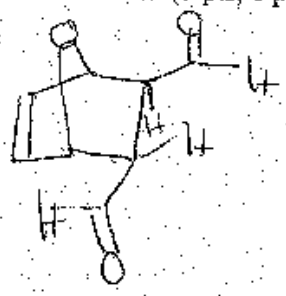


ox too far
-1

C. Short Answers part of Short Answers: (23 pts)

1. Given the following Diels Alder Reaction, give the correct product. Is the product which you drew (a) cis (trans) product from a cis (trans) dienophile (b) an endo (exo) product (c) not allowed because of the s-trans (s-cis) diene ? Circle one to all of the letters. (5 pts, 1 pt circling)



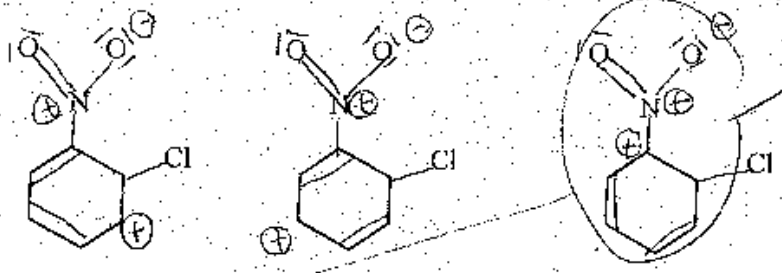


circled others -1

2 a. Given the following resonance structures, does the directing group shown act as a [(o,p activator) or (m deactivator)] (circle one entire parenthesis). (2pts each, 8 pts total)

2pt

said multiple directing -1



4pt

attempt -1

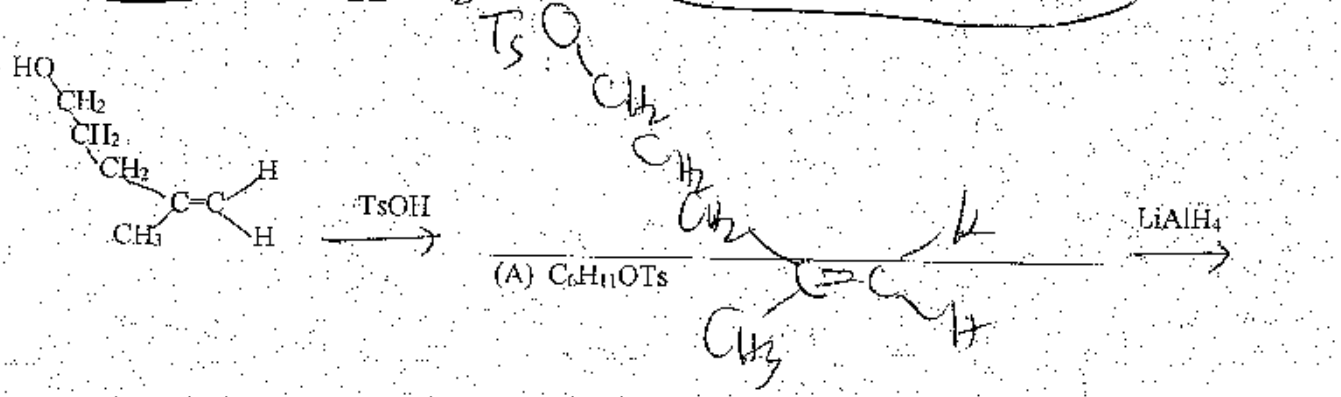
b. Which of the resonance structures determines the directing group effect which you chose above ? Circle the resonance structure and explain. You may circle more than one resonance structure and explain both resonance structures which you chose. (6 pts)

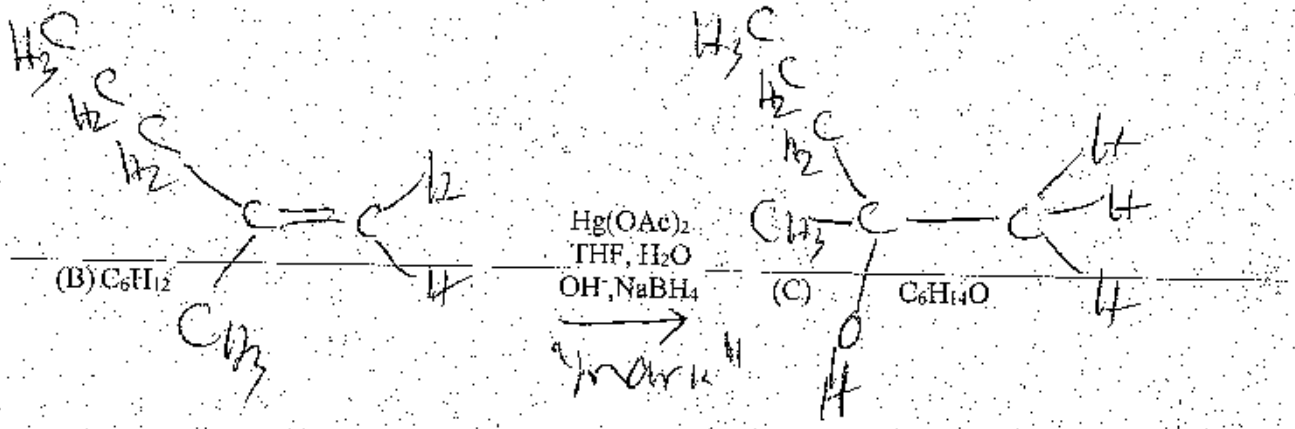
explain 2pt

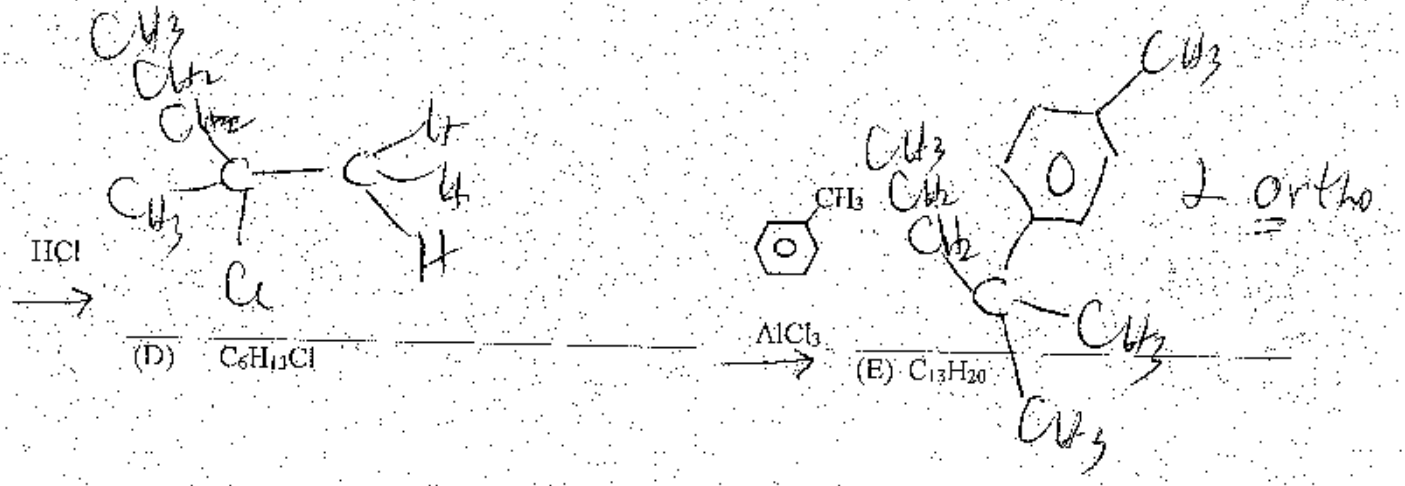
has a ⊕ next to ⊕ so it destabilize addition for NO_2 so that NO_2 directs to meta not o/p

3 Complete the following synthesis by filling in the blank. I have provided some hints to help you come up with the answers. NOTE: The way I grade this is for you to fill in reasonable molecules based on the immediate prior molecule. i.e. If you fill in part A with the wrong molecule and then do the next reaction to molecule B correctly you will get half credit for answering B correctly. If you fill in B with what you would have gotten if you got A correctly but which cannot possibly be generated from your wrong A, you will lose all credit even if it matches what you should have gotten. (There is no way that you can come up with this answer except perhaps by guessing.) (2 pts each, 10 pts total)

NL = not likely -1 SO - sort of OK

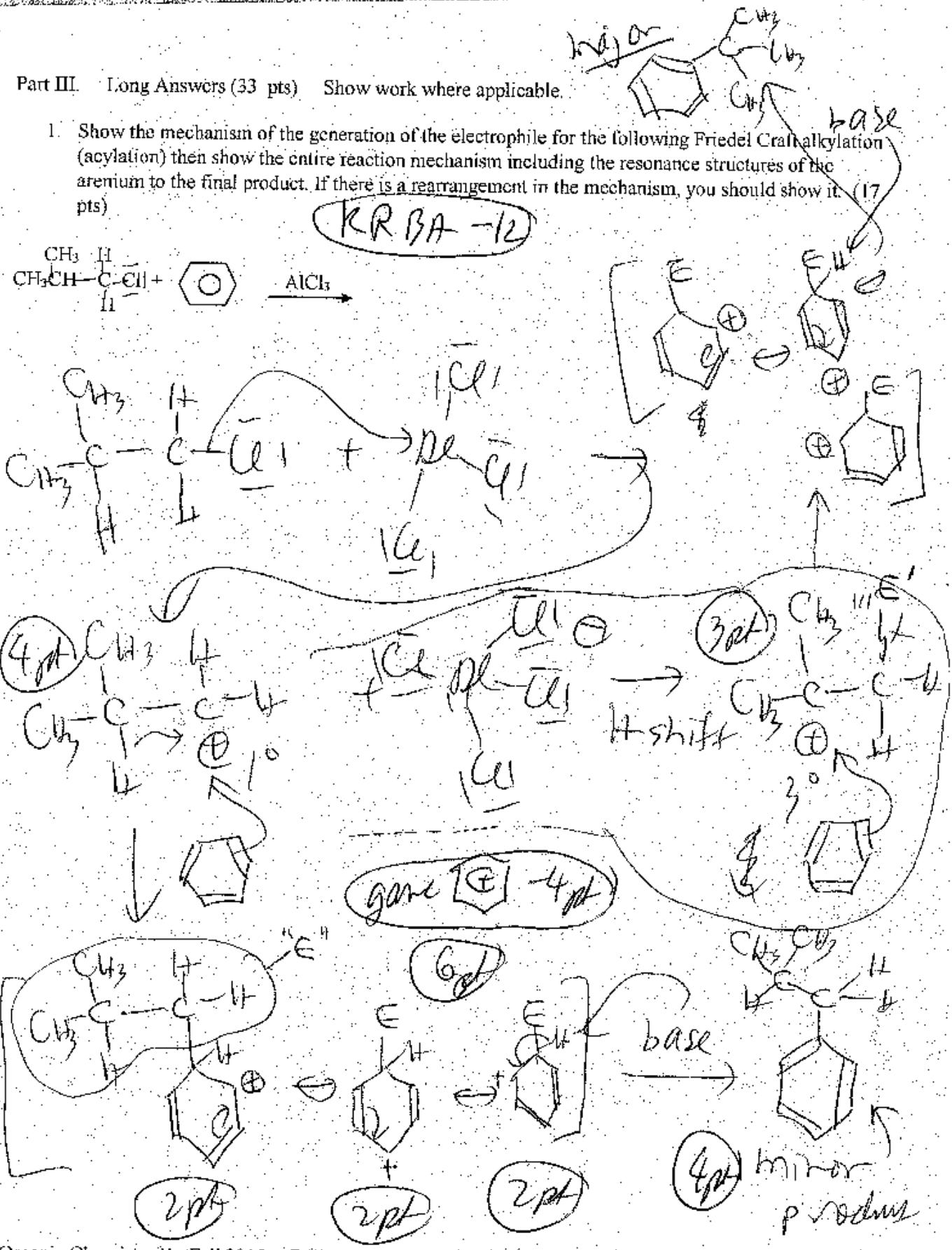




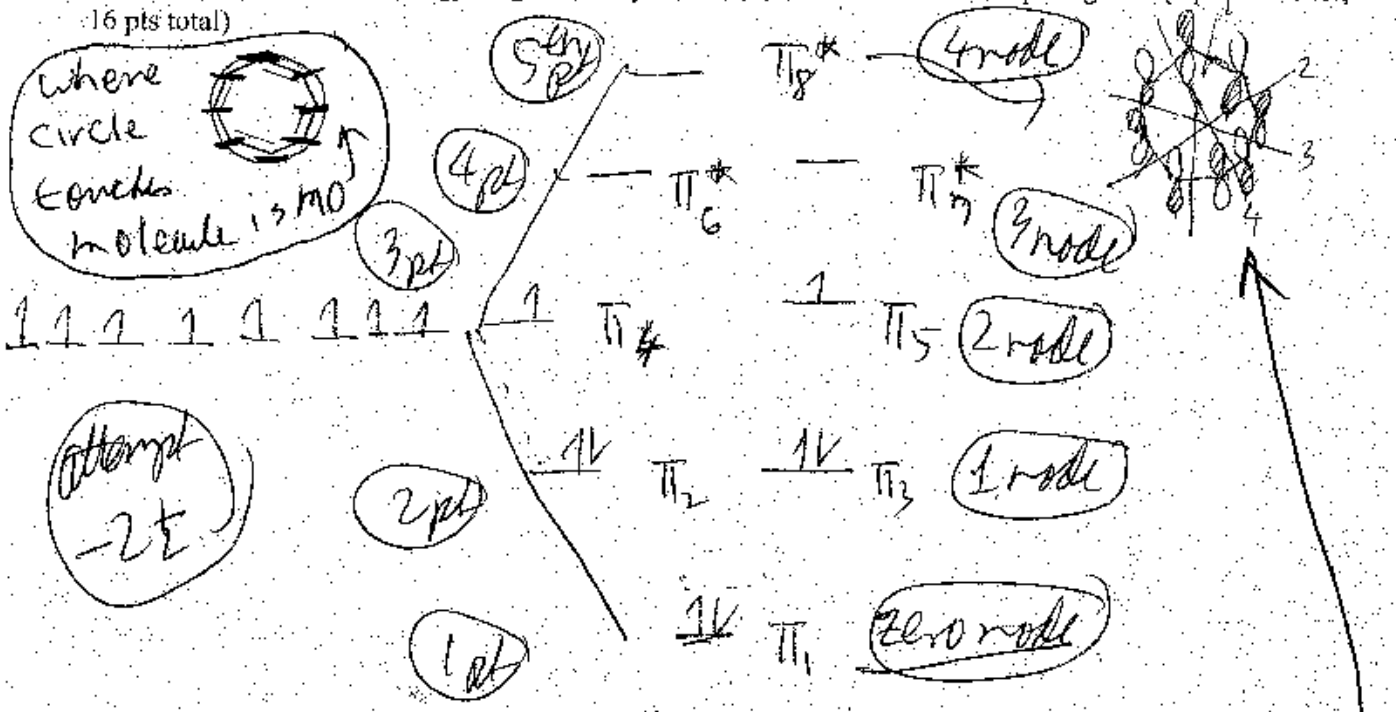


Part III. Long Answers (33 pts) Show work where applicable.

1. Show the mechanism of the generation of the electrophile for the following Friedel Craft alkylation (acylation) then show the entire reaction mechanism including the resonance structures of the arenium to the final product. If there is a rearrangement in the mechanism, you should show it. (17 pts)



2. (a) Draw the MO energy diagram for cyclocta-1,3,5,7-tetraene in the space given. (5 pts this letter, 16 pts total)



(b) Show the p orbital atomic orbital combination for the highest π* MO in your energy diagram above in part (a) by the MO which matches. Represent the math sign of your p orbital lobes by shading in one of the lobes in all of the p orbitals. Show the nodes. (3 pts)

attempt -1/2

asked for one not all 8

not highest -1 π_8^*

(c) Fill your MO energy diagram [which you drew above in (a)] with the appropriate number of electrons for the cyclocta-1,3,5,7-tetraene Use up and down arrows to represent electrons. (4 pts)

Consistent OK

attempt -2

(d) Show a Hückel rule explanation of the stability/instability of your cyclocta-1,3,5,7-tetraene (Hückel Rule is 4n+2 = # π electrons) (4 pts)

n = 3/2

$4n+2 = 8\ \bar{e}$ not aromatic

$4n = 8-2 = 6$

math -2

$4n = 6$

$n = \frac{6}{4} = \frac{3}{2}$

wrong # $\bar{e}$ -1

Organic Chemistry II (CHEM 442) MWF 12 Lecture Fall 2015 Dr. Hahn Exam II 10/26/15 M Form A

Sign Name _____ Print Name _____

Please show work for all questions for partial and full credit (except multiple choice questions) even on questions which do not specify work. Only answers which are clearly readable will be graded. If you write the answer other than in the intended space without clear indication of where, I will not grade it . (I am grading 250 x 10 page exams. by myself I am not going to spend 3 hours looking for your answer somewhere on the exam and I am not going to contact 250 people to tell me what they meant to write if I can't clearly read what you wrote. No Points for erased answers which are still somewhat visible. No points for errors going from the exam to the scantron. No Points for anything other than normal organic chemistry formulas showing enough information to answer the question. (2 pts print & sign name)

(total number of pages of the exam = 10 pages + periodic table + scantron Check number of pages. If you turn in less than 12 pages, it is your own responsiblity for not completing the exam.)

Part I Multiple Choice (2 pts each, 26 pts total) Fill in your answer on the hardcopy of the exam as backup for your scantron in case you erased so much that there is a computer error in grading.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

1) Which of the following compounds will undergo bromination least rapidly when treated with Br_2 and $FeBr_3$? 1) _____

A) acetanilide

B) p-methylacetanilide

C) benzenesulfonic acid

D) benzene

E) bromobenzene

2) Which of the following reagents is the best choice for oxidizing a primary alcohol to an aldehyde? 2) _____

A) $LiAlH_4$

B) DMSO, $(COCl)_2$, Et_3N (Swern)

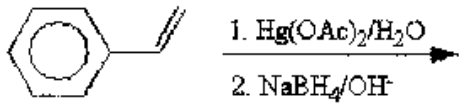
C) H_2CrO_4

D) $KMnO_4$

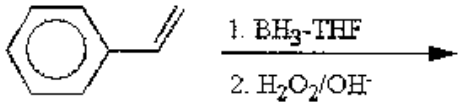
E) $Na_2Cr_2O_7$, H_2SO_4

3) Which of the following reactions will result in the formation of a secondary alcohol(s) in good yield? 3) _____

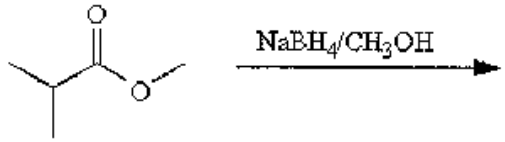
A)



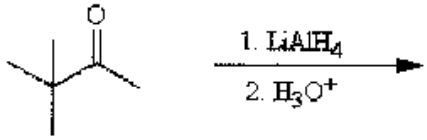
B)



C)



D)



E) both A and D

4) What type of orbital do the lone pair electrons on oxygen occupy in ethanol? 4) _____

A) sp^3 B) sp C) π D) p E) σ

5) What compound results when 1-butanol is treated with P/I_2? 5) _____

A) racemic $CH_3CH_2CHICH_3$

B) $CH_3CH_2CH_2CH_2OP(OH)_2$

C) $CH_3CH_2CH_2CH_2P/I_2$

D) $CH_3CH_2CH_2CH_2I$

E) Primary alcohols don't react with P/I_2.

6) What descriptive term is applied to the type of diene represented by 1,5-octadiene? 6) _____

A) isolated diene

B) alkynyl diene

C) conjugated diene

D) cumulated diene

E) none of the above

7) Which of the following compounds is the most reactive dienophile in a Diels–Alder reaction with 1,3–butadiene? 7) _____

A) CH_2--CH_2

B) CH_2=$CHOCH_3$

C) CH_3CH=$CHCH_3$

D) $(CH_3)_2C$=CH_2

E) CH_2=CHCHO

8) UV spectroscopy measures the energy required to promote an electron from the _____ molecular orbital to the _____ molecular orbital. 8) _____

A) lowest occupied, lowest unoccupied

B) lowest occupied, highest unoccupied

C) highest occupied, highest unoccupied

D) highest occupied, lowest unoccupied

E) None of the above

9) Which of the following is also an acceptable name for 3–nitrophenol? 9) _____

A) *p*–nitrophenol

B) *m*–nitrophenol

C) *o*–nitrophenol

D) hydroquinone

E) 3–cresol

10) Aromatic molecules contain _____ π electrons. 10) _____

A) unpaired

B) no

C) 4n (with n an integer)

D) 4n + 2 (with n an integer)

E) 4n + 1 (with n an integer)

11) In electrophilic aromatic substitution reactions a bromine substituent: 11) _____

A) is an activator and an o,p–director.

B) is a deactivator and an o,p–director.

C) is a deactivator and a m–director.

D) is an activator and a m–director.

E) none of the above

12) 2-Methylbutan-1-ol is classified as _____. 12) _____

A) an enol

B) a secondary alcohol

C) a primary alcohol

D) a phenol

E) a tertiary alcohol

13) What is the major difference between an antiaromatic and aromatic compound? 13) _____

A) Aromatic compounds cannot have a charged atom in the structure

B) The structure must be cyclic for aromatic but not antiaromatic compounds?

C) Antiaromatic compounds have at least one *sp*3 hybridized atom in the ring

D) Antiaromatic compounds can assume a chair-like structure while aromatic compounds are nearly flat

E) Only aromatic compounds follow Huckle's rule.

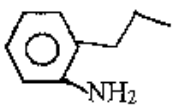
Please show work on all questions for partial credit even on questions which do not specify. Please write legibly. If I cannot read your answer, I cannot grade your answer. (use back of exam for scratch paper)

II. Short Answers (39 pts)

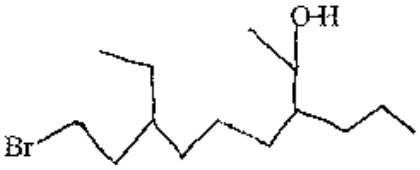
A. Nomenclature: (2 pts each, 8 pts)

1. Given the structural formula shown below, give the IUPAC name of the molecule.

a. name _____



b. name _____

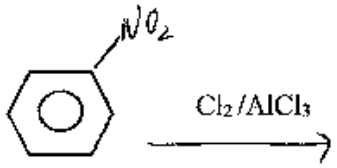


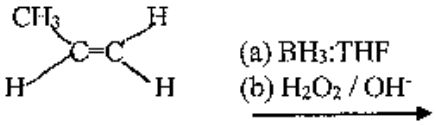
2. Given the following IUPAC name, draw a structural formula of the molecule (skeletal formula acceptable, condensed structure, Lewis Dot structure acceptable, molecular formula not acceptable - don't forget to show the hydrogens in your formula unless you are using the skeletal structure.)

a 2,3-dibromobenzoic acid

b Z-7-bromonon-3-en-3-ol

B. Reactions: Show the Organic Product in the following reactions by giving the structural formula of the product. (skeletal formula, condensed structure, Lewis Dot structure are all acceptable. Molecular Formula is **not** acceptable.) DO **NOT** SHOW MECHANISMS. You will only earn points for product which are correct or are regioisomers, or enantiomers of the correct product or is an intermediate on the way to produce the correct product. **I will give no points –zero points for anything else**. (2 pts each, 8 pts)

1) 

2) 

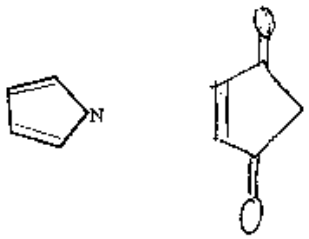
3) CH_3CH_2-O-H $\xrightarrow{PCl_5}$

4)

CH_3-CH_2-CH_2O-H $\xrightarrow{Na_2Cr_2O_7 / H^+}$

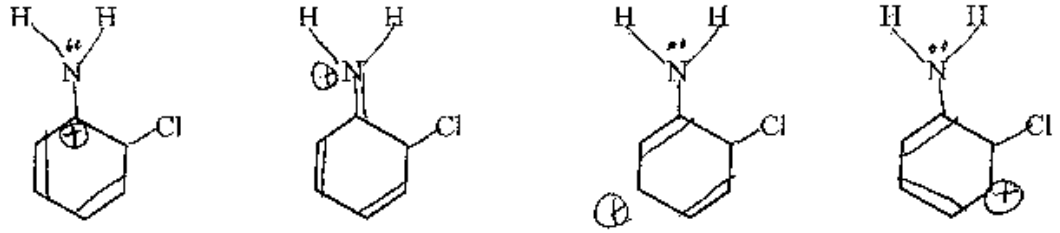
C. Short Answers part of Short Answers: (23 pts)

1. Given the following Diels Alder Reaction, give the correct product. Is the product which you drew (a) cis (trans) product from a cis (trans) dienophile (b) an endo (exo) product (c) not allowed because of the s-trans (s-cis) diene ? Circle one to all of the letters. (5 pts, 1 pt circling)



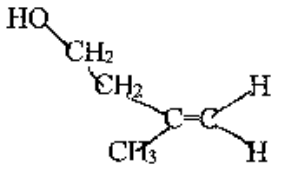
2 a. Given the following resonance structures, does the directing group shown act as a

[(o,p activator) or (m deactivator)] (circle one entire parenthesis). (4 pts each, 8 pts total)



b. Which of the resonance structures determines the directing group effect which you chose above ? Circle the resonance structure and explain. You may circle more than one resonance structure and explain both resonance structures which you chose. (4 pts)

3 Complete the following synthesis by filling in the blank. I have provided some hints to help you come up with the answers. NOTE: The way I grade this is for you to fill in reasonable molecules based on the immediate prior molecule. i.e. If you fill in part A with the wrong molecule and then do the next reaction to molecule B correctly you will get half credit for answering B correctly. If you fill in B with what you would have gotten if you got A correctly but which cannot possibly be generated from your wrong A, you will lose all credit even if it matches what you should have gotten. (There is no way that you can come up with this answer except perhaps by guessing.) (2 pts each, 10 pts total)



TsOH → (A) ~~C_4H_8OTs~~ C_5H_9OTs → CH_3O^-

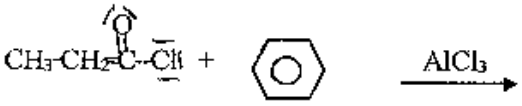
note: correct formula was projected on board from the start of class

(B) ~~$C_5H_{10}O_2$~~ $C_6H_{12}O$ → (BH_3 THF; H_2O_2, OH^-) → (C) ~~$C_5H_{12}O_2$~~ $C_6H_{14}O_2$

TsOH → (D) ~~$C_5H_{11}OTs$~~ $C_6H_{13}OOTs$ → $LiAlH_4$ → (E) ~~C_5H_{12}~~ $C_6H_{14}O$

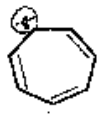
Part III. Long Answers (33 pts) Show work where applicable.

1. a. Show the mechanism of the generation of the electrophile for the following Friedel Craft alkylation (acylation) then show the entire reaction mechanism including the resonance structures of the arenium to the final product. If there is a rearrangement in the mechanism, you should show it. (14 pts, 17 pts total)



b. How would you use the product of the Friedel Craft acylation to attach a primary alkyl to benzene ? Why can't you just attach a primary alkyl group to a benzene using Friedel Craft Alkylation ? Explain. (3 pts)

2 (a) Draw the MO energy diagram for cyclohepta-1,3,5-trienyl cation in the space given. (5 pts this letter, 16 pts total)



(b) Show the p orbital atomic orbital combination for the highest π^* MO in your energy diagram above in part (a) by the MO which matches. Represent the math sign of your p orbital lobes by shading in one of the lobes in all of the p orbitals. Show the nodes. (3 pts)

(c) Fill your MO energy diagram [which you drew above in (a)] with the appropriate number of electrons for the cyclohepta-1,3,5-trienyl cation Use up and down arrows to represent electrons. (4 pts)

(d) Show a Huckel rule explanation of the stability/instability of your cyclohepta-1,3,5-trienyl cation (Huckel Rule is $4n+2 = \#\ \pi$ electrons) (4 pts)

n = _____

Organic Chemistry II (CHEM 442) MWF 12 Lecture Fall 2015 Dr. Hahn Exam II 10/26/15 M Form B

Sign Name_____Print Name _____

Please show work for all questions for partial and full credit (except multiple choice questions) even on questions which do not specify work. Only answers which are clearly readable will be graded. If you write the answer other than in the intended space without clear indication of where, I will not grade it . (I am grading 250 x 10 page exams. by myself I am not going to spend 3 hours looking for your answer somewhere on the exam and I am not going to contact 250 people to tell me what they meant to write if I can't clearly read what you wrote. No Points for erased answers which are still somewhat visible. No points for errors going from the exam to the scantron. No Points for anything other than normal organic chemistry formulas showing enough information to answer the question. (2 pts print & sign name) Color

(total number of pages of the exam = 10 pages + periodic table + scantron Check number of pages. If you turn in less than 12 pages, it is your own responsiblity for not completing the exam.)

Part I Multiple Choice (2 pts each, 26 pts total) Fill in your answer on the hardcopy of the exam as backup for your scantron in case you erased so much that there is a computer error in grading.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

1) Which of the following reagents is the best choice for oxidizing a primary alcohol to an aldehyde? 1) _____

A) $LiAlH_4$

B) DMSO, $(COCl)_2$, Et3N (Swern)

C) H_2CrO_4

D) $KMnO_4$

E) $Na_2Cr_2O_7$, H_2SO_4

2) Which of the following is also an acceptable name for 3-nitrophenol? 2) _____

A) *p*-nitrophenol

B) *m*-nitrophenol

C) *o*-nitrophenol

D) hydroquinone

E) 3-cresol

3) What descriptive term is applied to the type of diene represented by 1,5-octadiene? 3) _____

A) isolated diene

B) alkynyl diene

C) conjugated diene

D) cumulated diene

E) none of the above

4) Aromatic molecules contain _____ π electrons. 4) _____

A) unpaired

B) no

C) 4n (with n an integer)

D) 4n + 2 (with n an integer)

E) 4n + 1 (with n an integer)

5) In electrophilic aromatic substitution reactions a bromine substituent: 5) _____

A) is an activator and an o,p–director.

B) is a deactivator and an o,p–director.

C) is a deactivator and a m–director.

D) is an activator and a m–director.

E) none of the above

6) What type of orbital do the lone pair electrons on oxygen occupy in ethanol? 6) _____

A) sp^3 B) sp C) π D) p E) σ

7) What compound results when 1–butanol is treated with P/I_2? 7) _____

A) racemic $CH_3CH_2CHICH_3$

B) $CH_3CH_2CH_2CH_2OP(OH)_2$

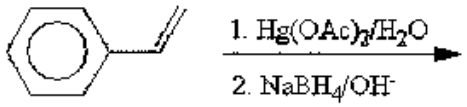
C) $CH_3CH_2CH_2CH_2P$

D) $CH_3CH_2CH_2CH_2I$

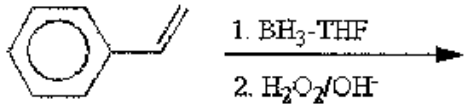
E) Primary alcohols don't react with P/I_2.

8) Which of the following reactions will result in the formation of a secondary alcohol(s) in good yield? 8) _____

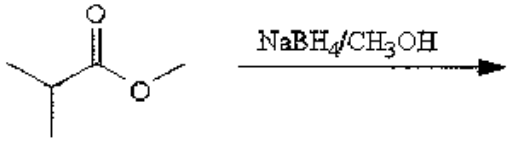
A)



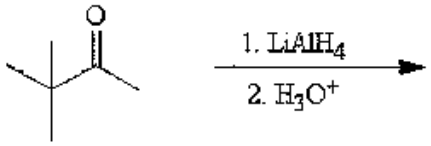
B)



C)



D)



E) both A and D

9) UV spectroscopy measures the energy required to promote an electron from the _____ molecular orbital to the _____ molecular orbital. 9) _____

A) lowest occupied, lowest unoccupied

B) lowest occupied, highest unoccupied

C) highest occupied, highest unoccupied

D) highest occupied, lowest unoccupied

E) None of the above

10) 2-Methylbutan-1-ol is classified as _____. 10) _____

A) an enol

B) a secondary alcohol

C) a primary alcohol

D) a phenol

E) a tertiary alcohol

11) What is the major difference between an antiaromatic and aromatic compound? 11) _____

A) Aromatic compounds cannot have a charged atom in the structure

B) The structure must be cyclic for aromatic but not antiaromatic compounds?

C) Antiaromatic compounds have at least one *sp*3 hybridized atom in the ring

D) Antiaromatic compounds can assume a chair-like structure while aromatic compounds are nearly flat

E) Only aromatic compounds follow Huckle's rule.

12) Which of the following compounds will undergo bromination least rapidly when treated with Br_2 and $FeBr_3$? 12) _____

A) acetanilide

B) p-methylacetanilide

C) benzenesulfonic acid

D) benzene

E) bromobenzene

13) Which of the following compounds is the most reactive dienophile in a Diels-Alder reaction with 1,3-butadiene? 13) _____

A) $CH_2{=}CH_2$

B) $CH_2{=}CHOCH_3$

C) $CH_3CH{-}CHCH_3$

D) $(CH_3)_2C{=}CH_2$

E) $CH_2{=}CHCHO$

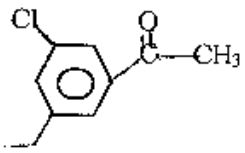
Please show work on all questions for partial credit even on questions which do not specify. Please write legibly. If I cannot read your answer, I cannot grade your answer. (use back of exam for scratch paper)

II. Short Answers (39 pts)

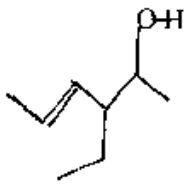
A. Nomenclature: (2 pts each, 8 pts)

1. Given the structural formula shown below, give the IUPAC name of the molecule.

a. name _____



b. name _____

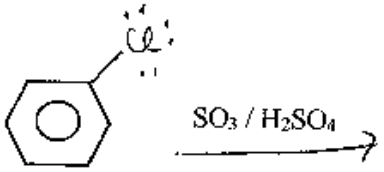


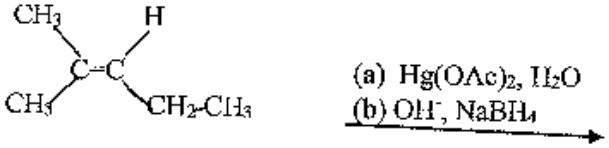
2. Given the following IUPAC name, draw a structural formula of the molecule (skeletal formula acceptable, condensed structure, Lewis Dot structure acceptable, molecular formula not acceptable - don't forget to show the hydrogens in your formula unless you are using the skeletal structure.)

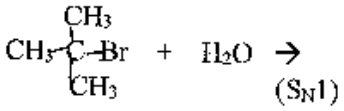
a m-nitroaniline

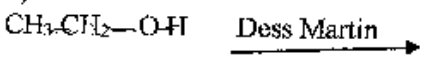
b 4,5-dimethyl-2-heptanol

B. Reactions: Show the Organic Product in the following reactions by giving the structural formula of the product. (skeletal formula, condensed structure, Lewis Dot structure are all acceptable. Molecular Formula is **not** acceptable.) DO **NOT** SHOW MECHANISMS. You will only earn points for product which are correct or are regioisomers, or enantiomers of the correct product or is an intermediate on the way to produce the correct product. **I will give no points –zero points for anything else.** (2 pts each, 8 pts)

1) 

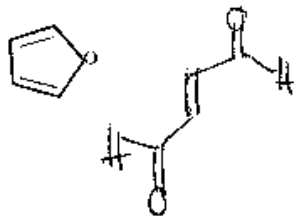
2) 

3) 

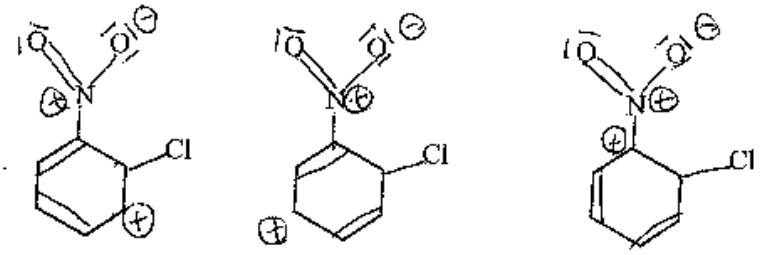
4) 

C. Short Answers part of Short Answers: (23 pts)

1. Given the following Diels Alder Reaction, give the correct product. Is the product which you drew (a) cis (trans) product from a cis (trans) dienophile (b) an endo (exo) product (c) not allowed because of the s-trans (s-cis) diene ? Circle one to all of the letters. (5 pts, 1 pt circling)

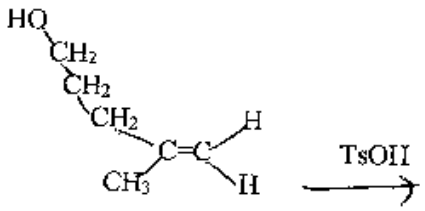


2 a. Given the following resonance structures, does the directing group shown act as a [(o,p activator) or (m deactivator)] (circle one entire parenthesis). (2pts each, 8 pts total)



b. Which of the resonance structures determines the directing group effect which you chose above ? Circle the resonance structure and explain. You may circle more than one resonance structure and explain both resonance structures which you chose. (6 pts)

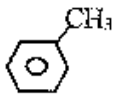
3 Complete the following synthesis by filling in the blank. I have provided some hints to help you come up with the answers. NOTE: The way I grade this is for you to fill in reasonable molecules based on the immediate prior molecule. i.e. If you fill in part A with the wrong molecule and then do the next reaction to molecule B correctly you will get half credit for answering B correctly. If you fill in B with what you would have gotten if you got A correctly but which cannot possibly be generated from your wrong A, you will lose all credit even if it matches what you should have gotten. (There is no way that you can come up with this answer except perhaps by guessing.) (2 pts each, 10 pts total)



TsOH → (A) $C_6H_{11}OTs$ → $LiAlH_4$ →

(B) C_6H_{12} → $Hg(OAc)_2$, THP, H_2O, OH^-, $NaBH_4$ → (C) $C_6H_{14}O$

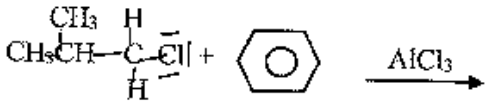
HCl →



(D) $C_6H_{13}Cl$ → $AlCl_3$ → (E) $C_{13}H_{20}$

Part III. Long Answers (33 pts) Show work where applicable.

1. Show the mechanism of the generation of the electrophile for the following Friedel Craft alkylation (acylation) then show the entire reaction mechanism including the resonance structures of the arenium to the final product. If there is a rearrangement in the mechanism, you should show it. (17 pts)



2 . (a) Draw the MO energy diagram for cyclocta-1,3,5,7-tetraene in the space given. (5 pts this letter, 16 pts total)

(b) Show the p orbital atomic orbital combination for the highest π^* MO in your energy diagram above in part (a) by the MO which matches. Represent the math sign of your p orbital lobes by shading in one of the lobes in all of the p orbitals. Show the nodes. (3 pts)

(c) Fill your MO energy diagram [which you drew above in (a)] with the appropriate number of electrons for the . cyclocta-1,3,5,7-tetraene Use up and down arrows to represent electrons. (4 pts)

(d) Show a Huckel rule explanation of the stability/instability of your cyclocta-1,3,5,7-tetraene (Huckel Rule is 4n+2 = # π electrons) (4 pts)

n = _____