Chem 5.12 Fall
Exam #4 Dec 3, 2008

Prof. B. Imperiali
Prof. S. O'Connor

PRINTED NAME KEY.

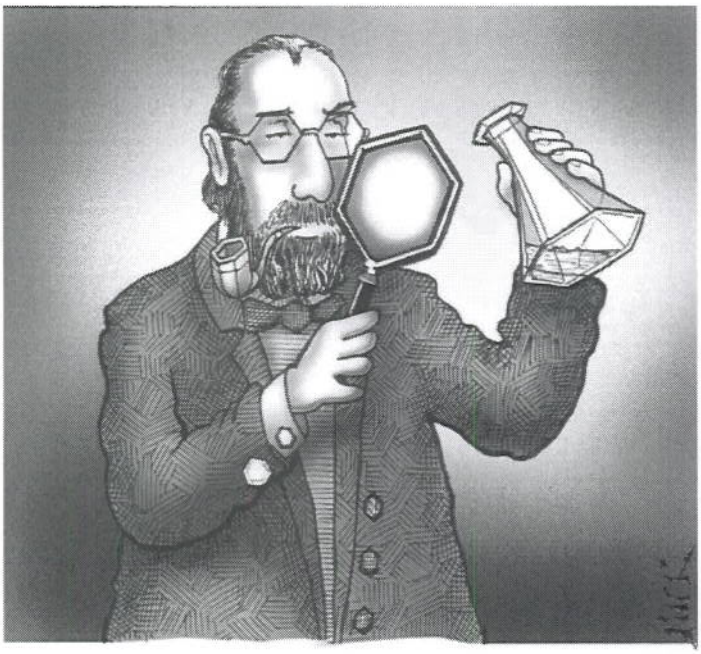
SIGNATURE TO POST

RECITATION TA _____

Guidelines:

- Take a minute to look through the exam before you start.
- Suggested times for questions shown in the table.
- We recommend that you start with the short questions to get your mind working.
- There are 13 numbered pages, one blank page for rough work, a periodic table and a table of electronegativity values in this exam. Please check that all pages are present before starting.
- Make sure you carefully read the instructions for each question.
- Make your answers as clear and neat as possible; it is far easier to assign partial credit if we can work through what you have presented.

Great events in Chemistry...



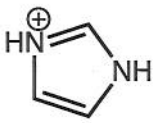
1865: Kekulé, moments before his brilliant insight into the structure of benzene.

1-10 (36 pts) 15 min	
11 (12 pts) 6 min	
12 (18 pts) 10 min	
13 (18 pts) 10 min	
14 (16 pts) 9 min	
Sub-Total	
BONUS (5)	
TOTAL out of 100	

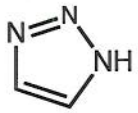
Good luck!!

Short questions (1-4; 3 points each) Name_____

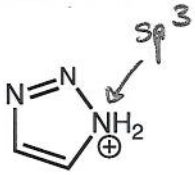
1. Which <u>one</u> of the following heterocycles does NOT show aromatic stabilization in the ionization state indicated?



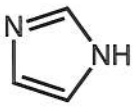
A



B



C



D

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2. What is the approximate energy of the aromatic stabilization of benzene?
IDENTIFY THE VALUE AND THE CORRECT UNITS

10 cal/mol	35 kcal/mol	35 cal/mol	10 kcal/mol
A	B	C	D

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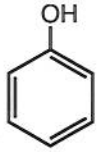
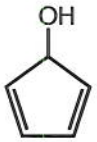
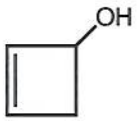
3. Which of the following compounds is MOST likely to lose H_2O upon treatment with H_2SO_4 (a source of H^+)?



A



B



C

D

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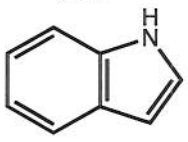
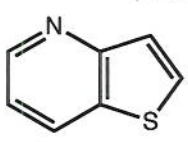
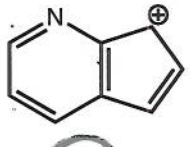
4. Which ONE of the following is NOT a 10-electron AROMATIC system?



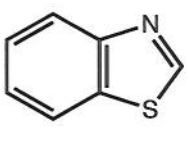
A



B



C

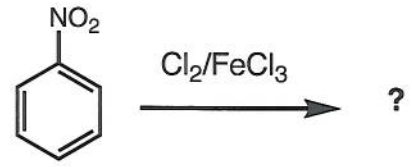


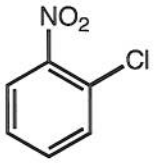
D

score

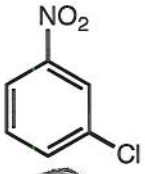
Short questions (5-6; 4 points each) Name_____

5. Identify the MAJOR product of the reaction shown?

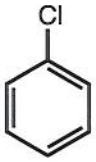




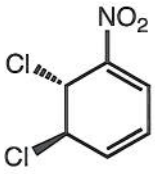
A



B



C



D

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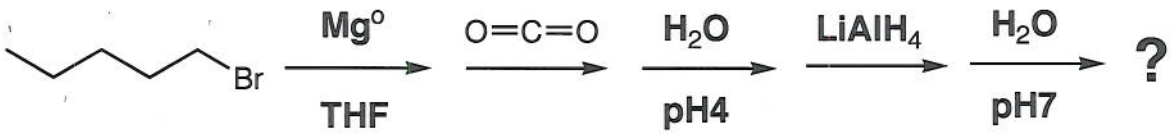
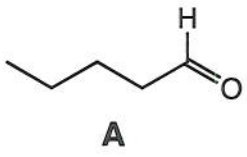
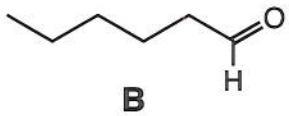
6. What is the FINAL product of the reaction sequence shown below?

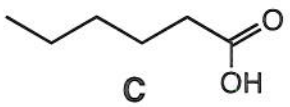




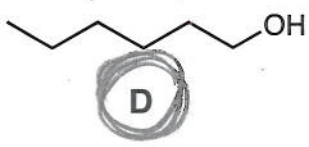
A



B



C

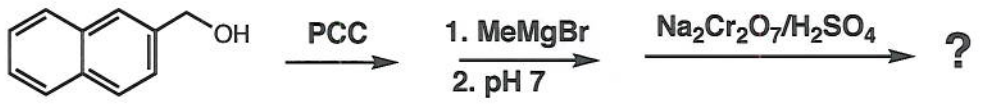


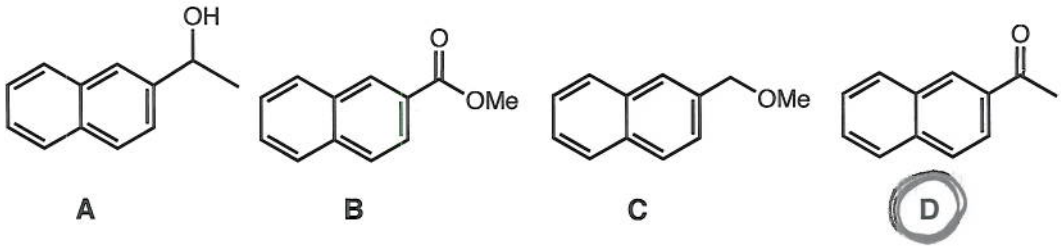
D

score

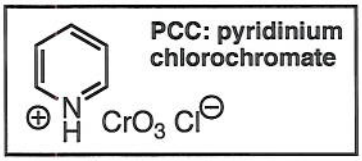
Short questions (7-8; 4 points each) Name_____

7. What is the FINAL product of the reaction sequence shown?





A B C D



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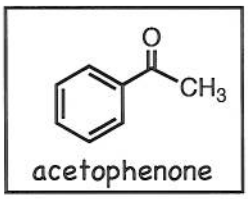
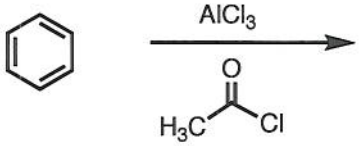
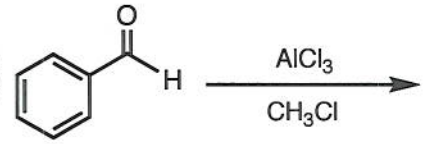
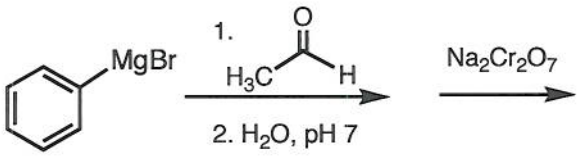
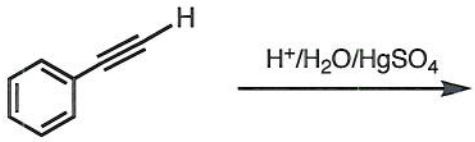
8. Which of the following reaction sequences does NOT give acetophenone as the MAJOR product?



A 

B 

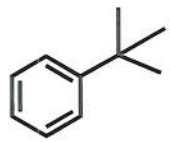
C 

D 

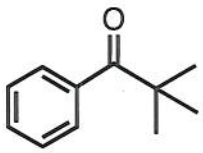
score

Short questions (9-10; 4 points each) Name_____

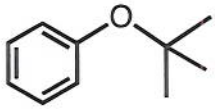
9. Rank the following compounds in order of reactivity in ELECTROPHILIC aromatic substitution.



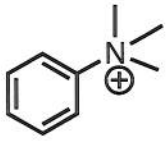
[2]



[3]



[1]



[4]

Rank the MOST REACTIVE as 1 and the LEAST REACTIVE as 4

All correct = (4)

1,4 OR 2,3 OR 1,2 or 3,4 correct (2)

1 OR 4 correct (1)

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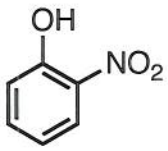
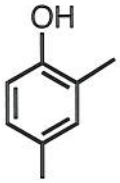
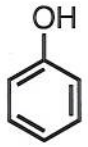
10. Rank the following in terms of acidity. Show the MOST ACIDIC as 1 and the LEAST ACIDIC as 4.



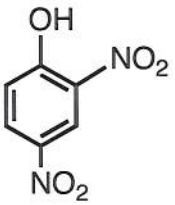
[2]



[4]



[3]



[1]

All correct = (4)

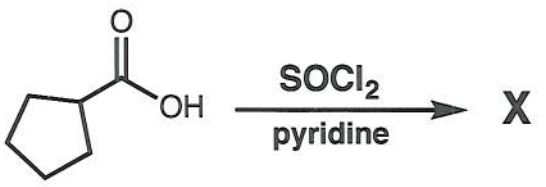
1,4 2,3 1,2 OR 3,4 correct (2)

1 OR 4 correct (1)

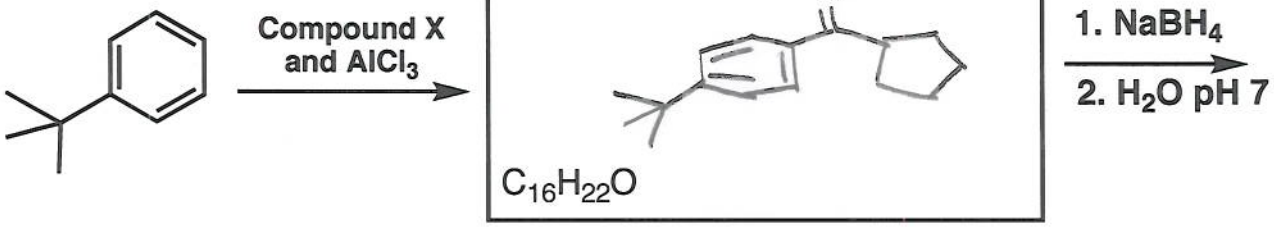
score

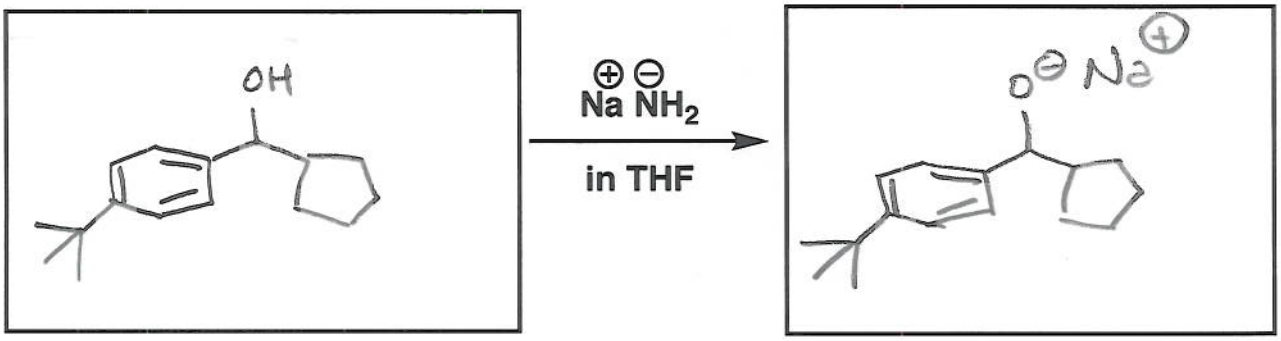
Long questions (points as indicated) Name_____

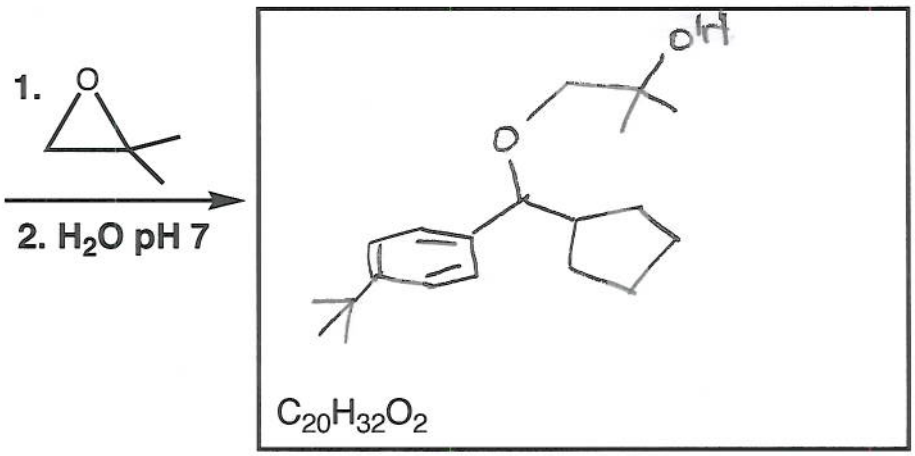
11. (12 points) Give the structures of the compounds in the boxes.



show MAJOR product





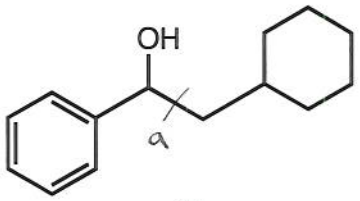


Make sure that the molecular formulas match your answer wherever they are provided!

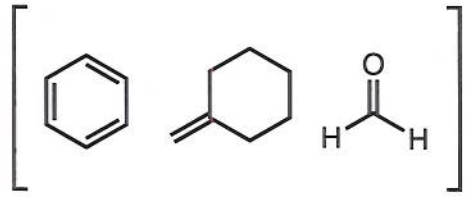
score

Long questions (Points as shown) Name _____

12. (18 points) Design a synthesis of compound Z.
The ONLY carbon-containing starting materials that you can use are shown in the square brackets next to the target. You may use any other common reagents (e.g. oxidants, reductants, Lewis acids, metals, and thionyl chloride) and solvents. NO need to show mechanisms!

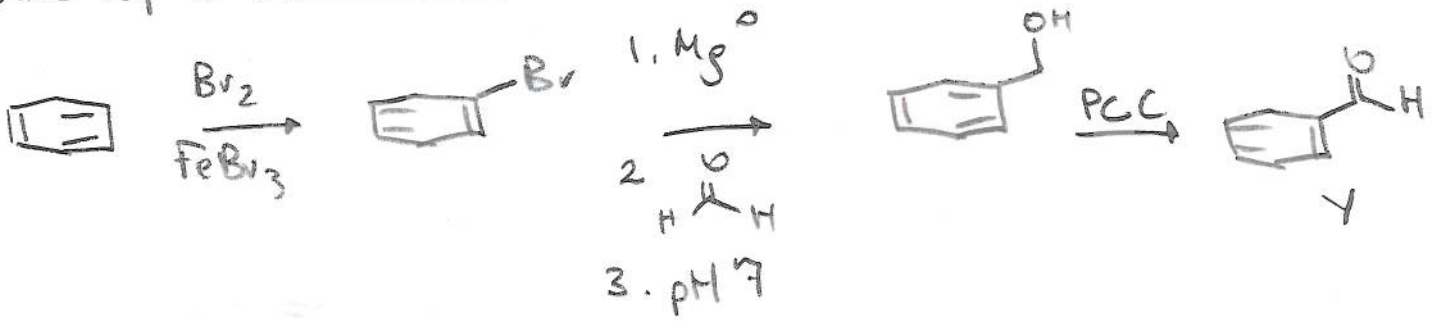


Z

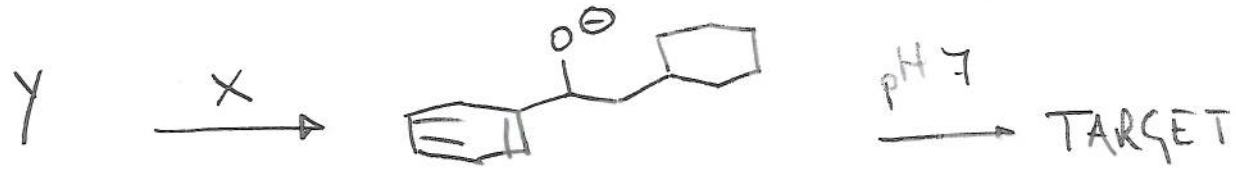


Note: A retrosynthetic analysis will be useful for figuring this problem out.

Route #1 a disconnection



then



OR

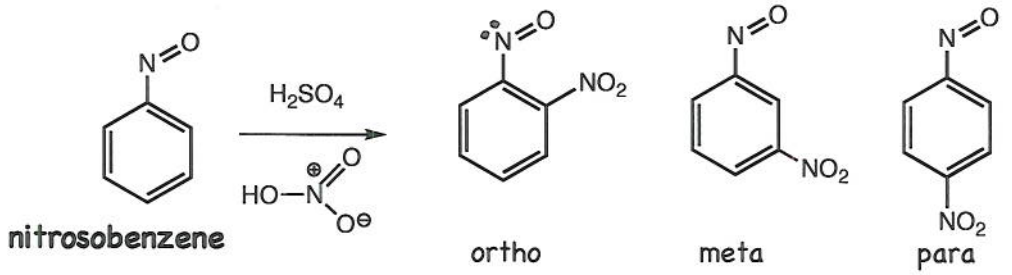
+ oxidize.

score

Long questions (Points as shown) Name_____

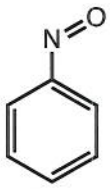
13. (18 points) Nitrosobenzene undergoes electrophile aromatic substitution (EAS) when treated with nitric acid and sulfuric acid. (This question continues on p.9.)

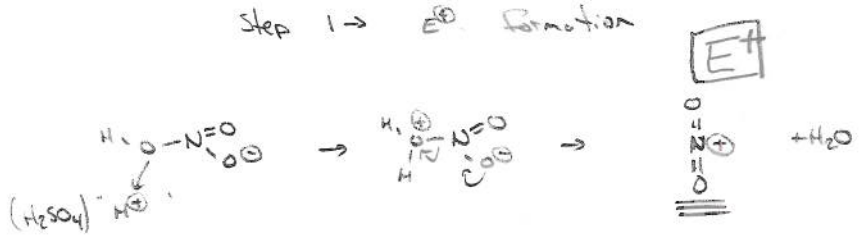
a) (12 points) DEDUCE whether the nitroso group is "ortho/para" OR "meta" directing by comparing the mechanisms for para and meta substitution.

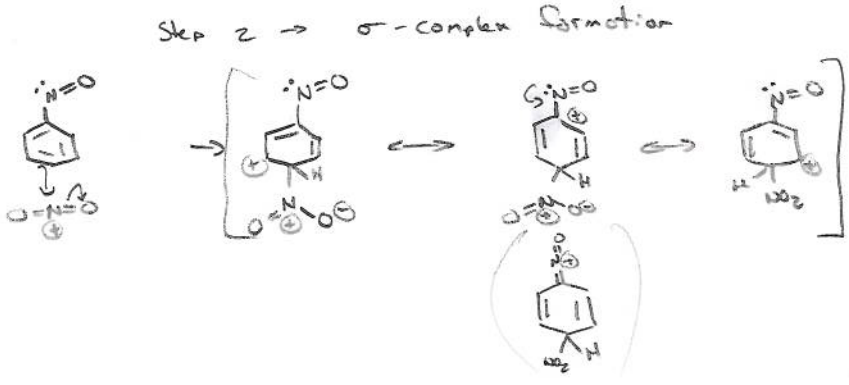


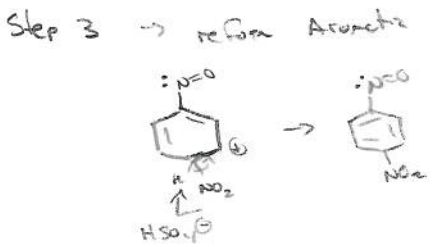
For full credit you must show the detailed stepwise mechanism, including all arrows, the structure of the key electrophile and all resonance structures of the key intermediates. Be sure to show all three steps in the EAS reaction.

Mechanism for para substitution:









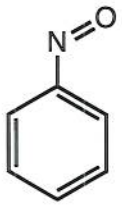
score

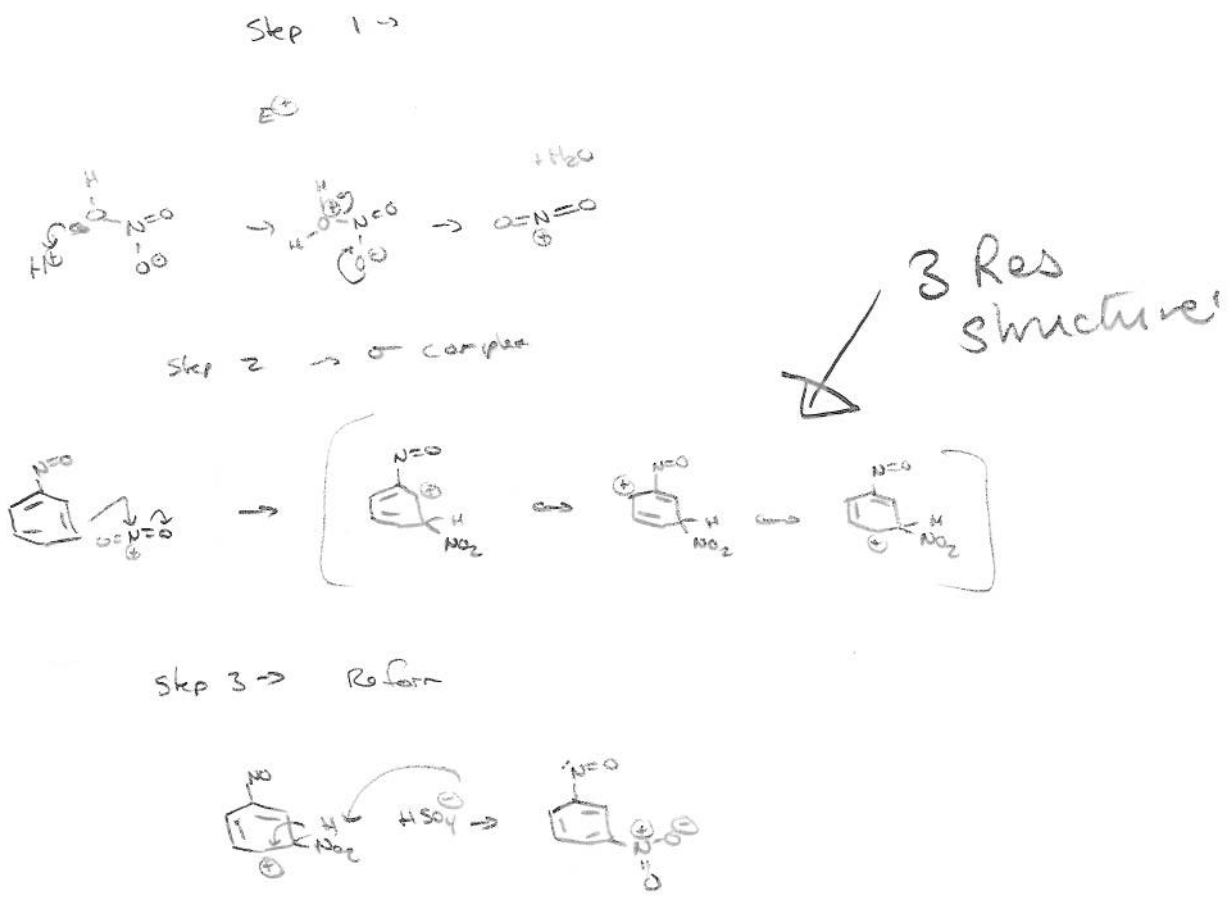
6

Long questions (Points as shown) Name_____

13 a) (contd.)

Mechanism for meta substitution





For para substitution there are 4 possible resonance structures for the σ complex, but for meta substitution the are only 3

o/p favored

score

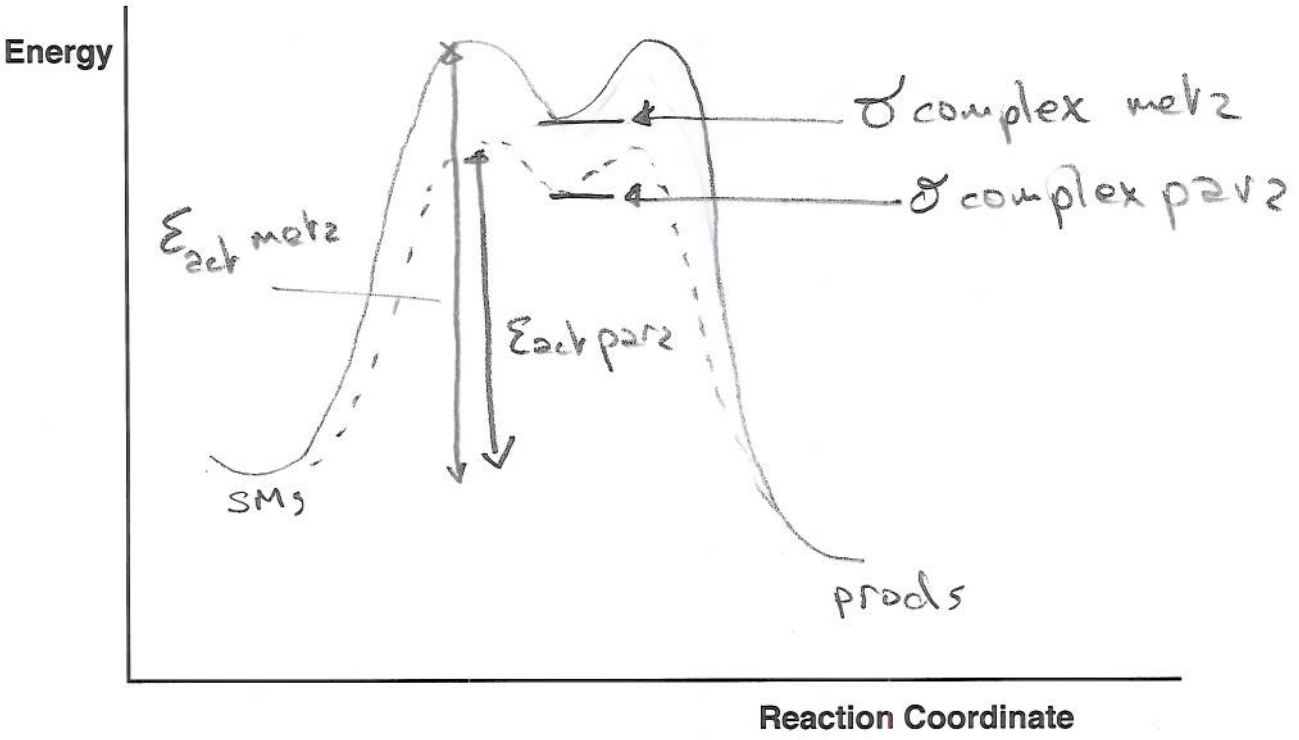
6

13. (contd. 6 points) b) Assuming that the OVERALL reaction is slightly EXOTHERMIC - construct an energy diagram for the EAS reaction of nitrosobenzene leading to the para- and meta-substituted products.

The diagram MUST show:

- The relative energies of the starting material, the σ-complexes and the products.

- The energies of activation for the rate determining steps of the para- and meta-directing EAS processes.



Note: No need to draw out structures - just labels such as SM, PROD, σ-COMPLEX. are fine.

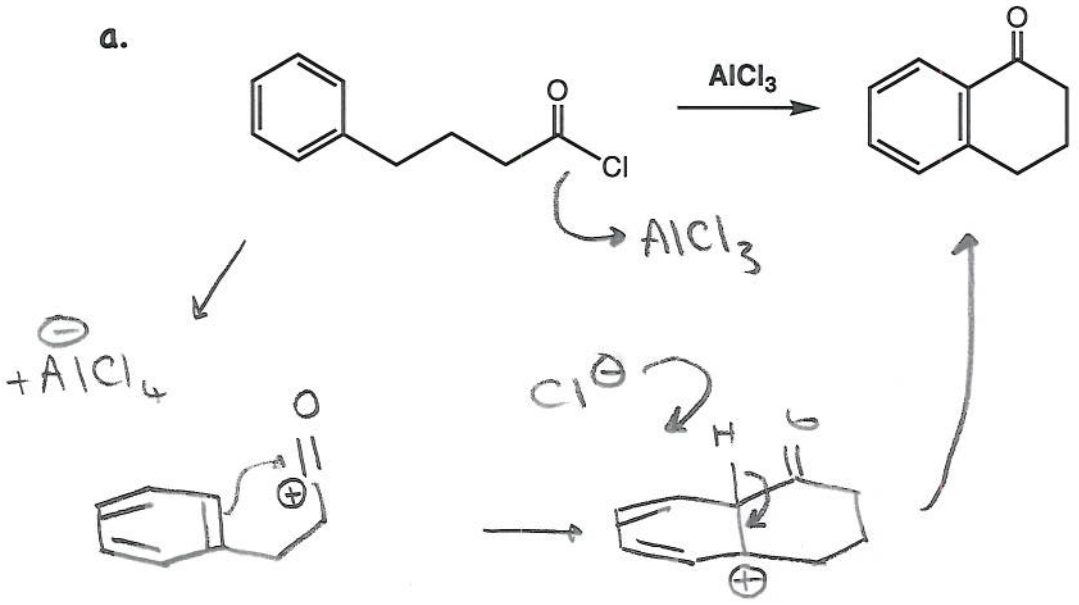
score

Long questions (Points as shown)

Name _____

15. (16 points) Provide the detailed stepwise mechanisms for the following transformations.

a.



$$AlCl_4^{\ominus} \rightleftharpoons AlCl_3 + Cl^{\ominus}$$

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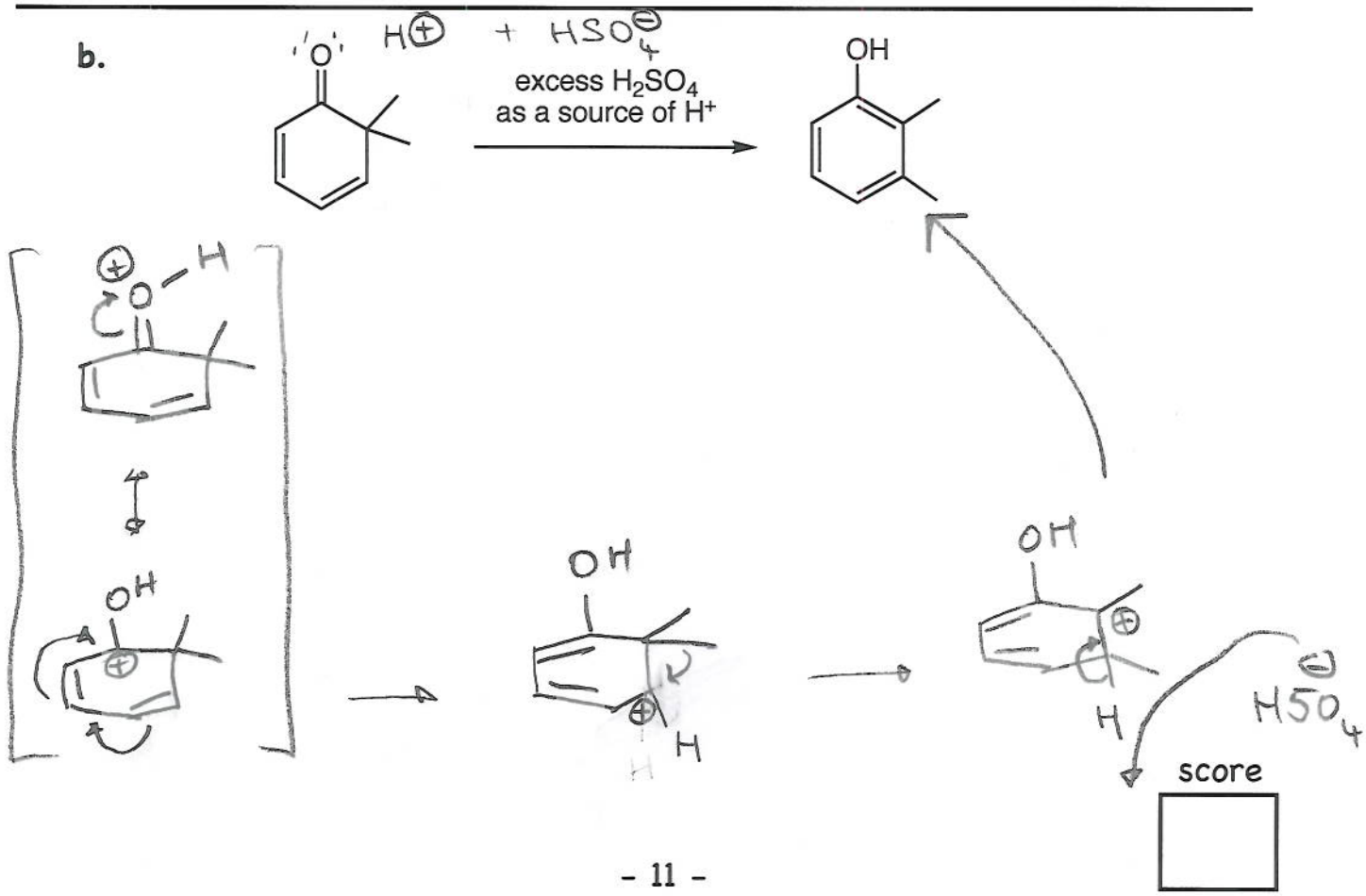
b.



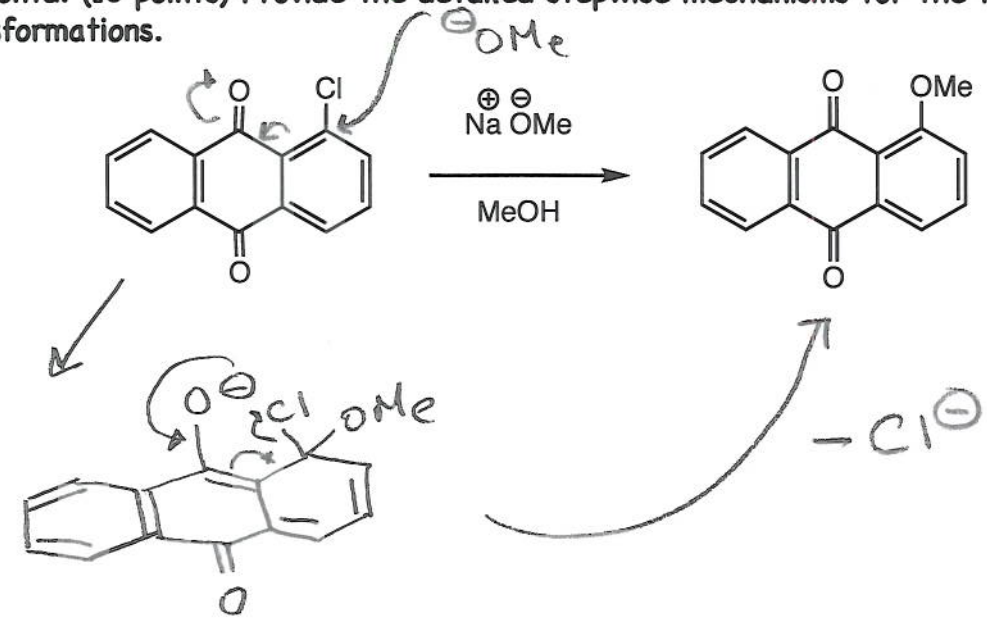
score

Long questions (Points as shown)

Name _____

15. Contd. (16 points) Provide the detailed stepwise mechanisms for the following transformations.

c.



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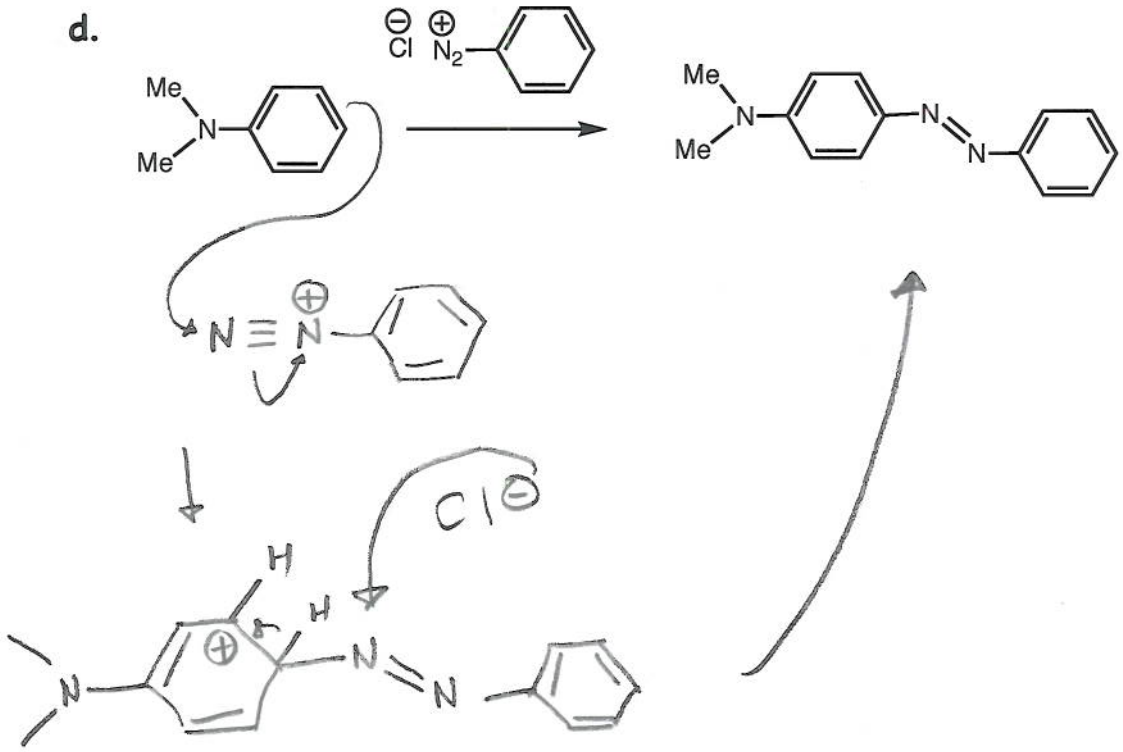
d.



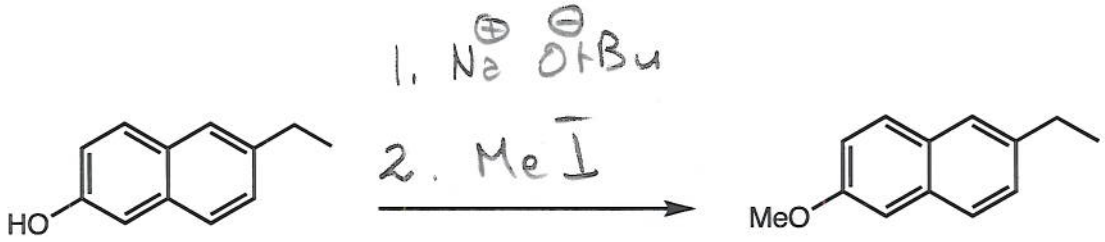
Hint: Write out the Lewis structure for the compound above the arrow.

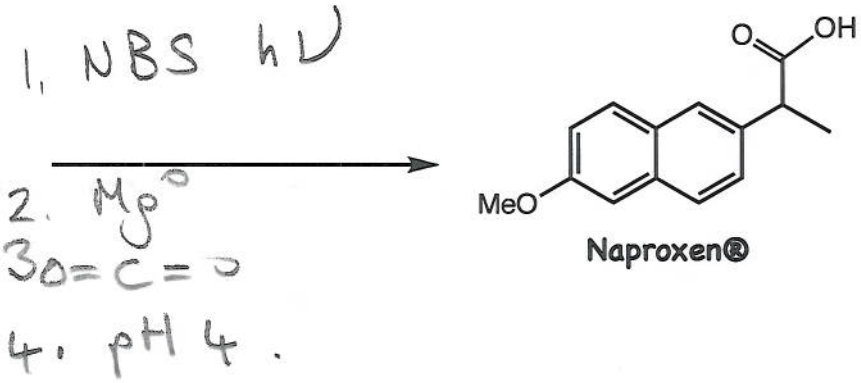
score

BONUS QUESTION (5 points) Name _____

The following represents part of a synthetic route to Naproxen® (sold under the trade-name Aleve), which is an important anti-inflammatory agent.

Provide the best reagents for each transformation (more than one step may be required). No need to show mechanisms!





Naproxen®

score