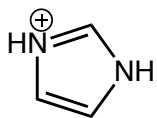


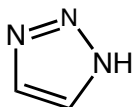
Short questions (1-4; 3 points each)

Name _____

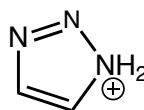
1. Which one of the following heterocycles does NOT show aromatic stabilization in the ionization state indicated?



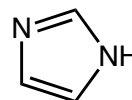
A



B



C



D

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

10 cal/mol

A

35 kcal/mol

B

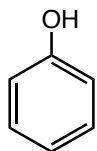
35 cal/mol

C

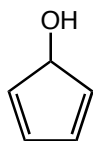
10 kcal/mol

D

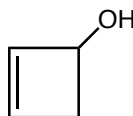
3. Which of the following compounds is MOST likely to lose H₂O upon treatment with H₂SO₄ (a source of H⁺)?



A



B

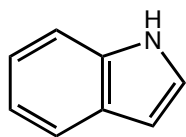


C



D

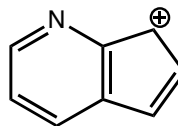
4. Which ONE of the following is NOT a 10-electron AROMATIC system?



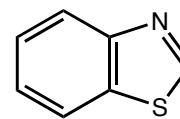
A



B



C



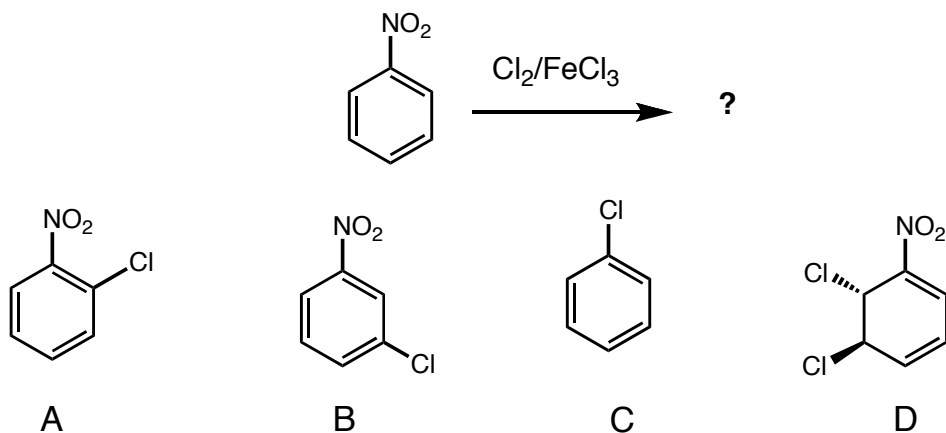
D

score

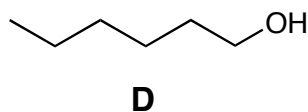
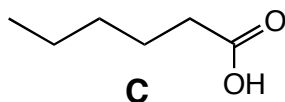
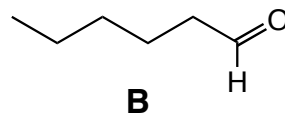
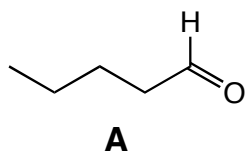
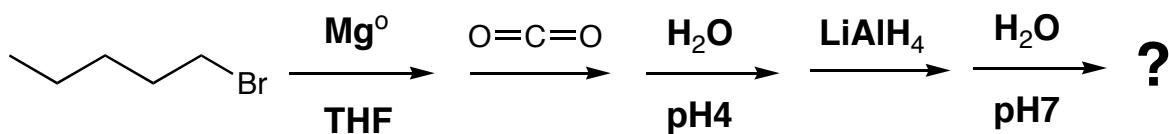
Short questions (5-6; 4 points each)

Name _____

5. Identify the MAJOR product of the reaction shown?



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

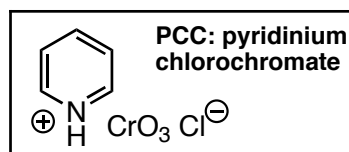
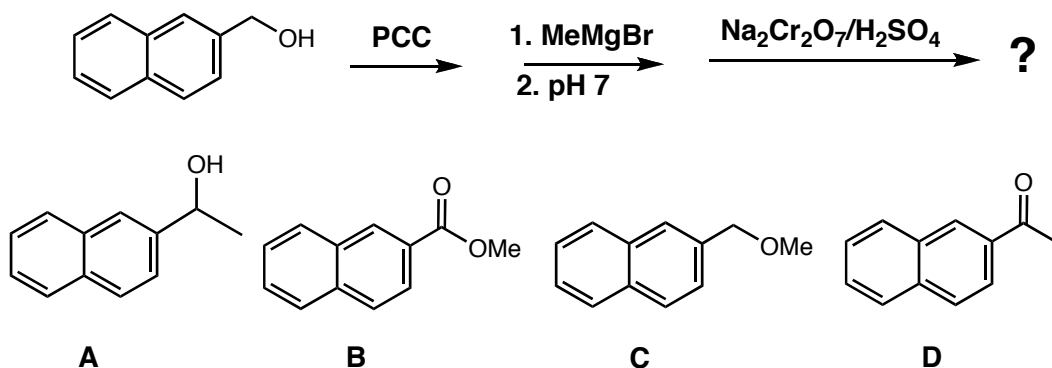


score

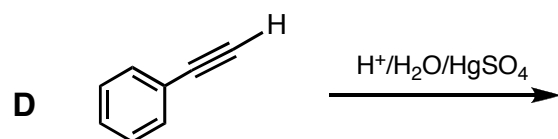
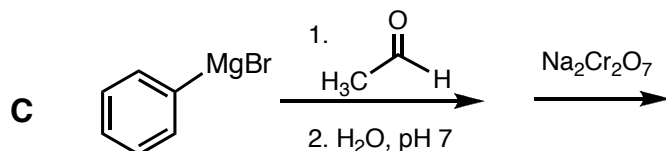
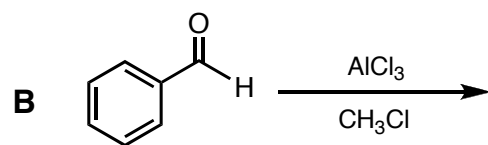
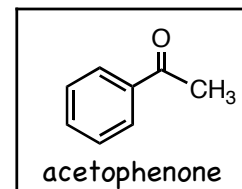
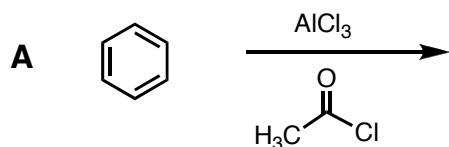
Short questions (7-8; 4 points each)

Name _____

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



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

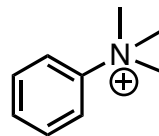
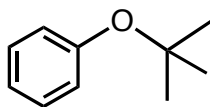
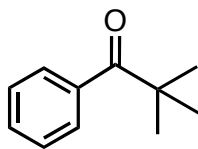
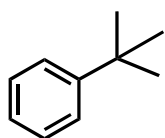


score

Short questions (9-10; 4 points each)

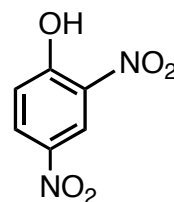
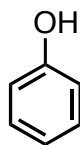
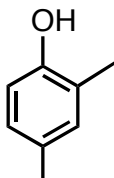
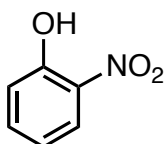
Name _____

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



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

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

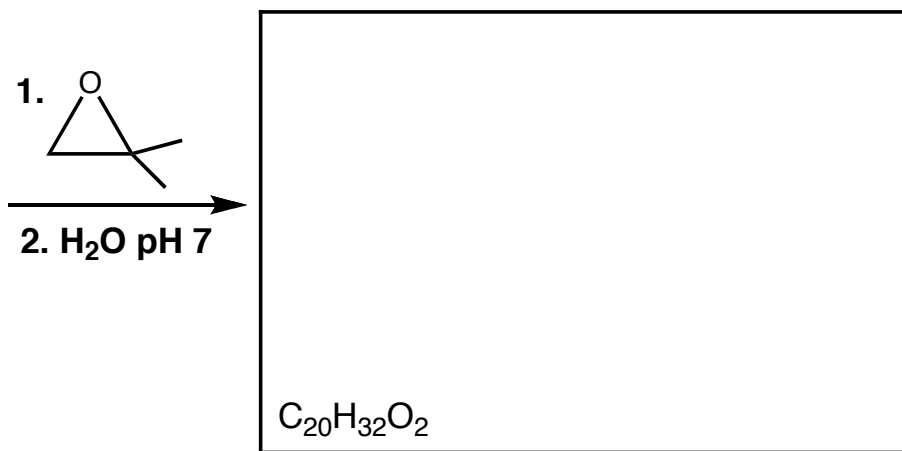
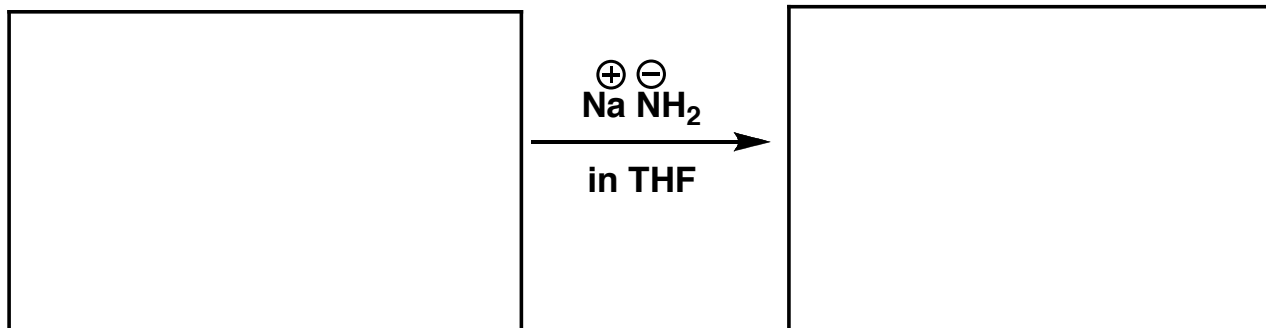
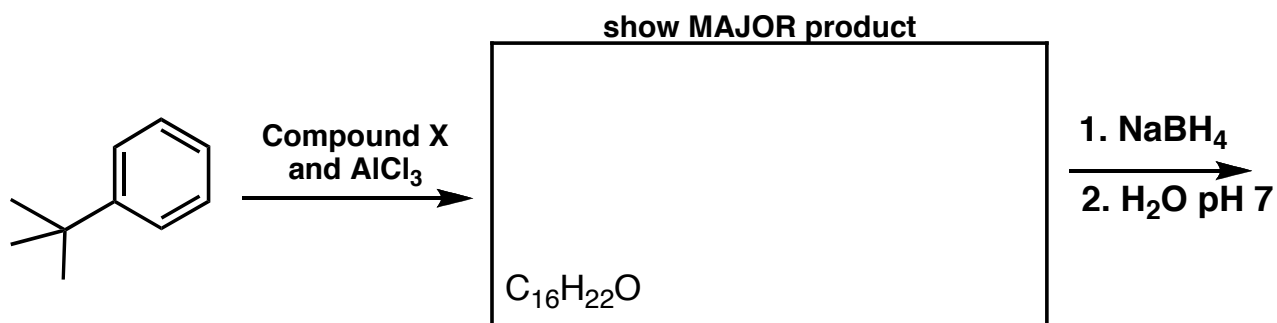
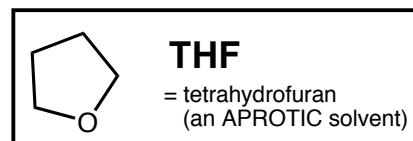
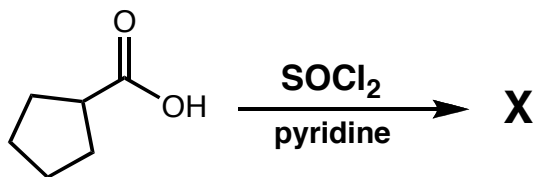


score

Long questions (points as indicated)

Name _____

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

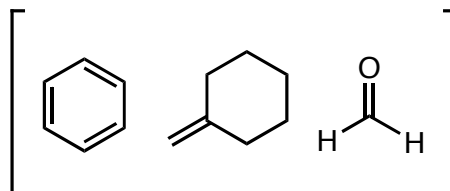
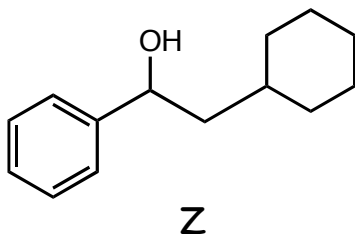


Make sure that the molecular formulas match your answer wherever they are provided!

score

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!

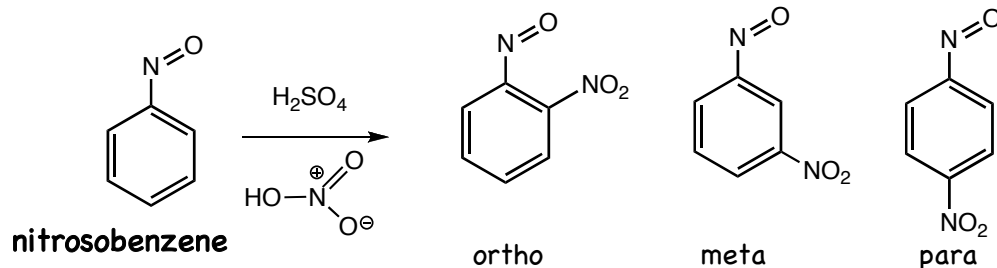


Note: A retrosynthetic analysis will be useful for figuring this problem out.

score

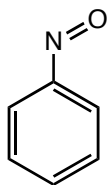
13. (18 points) Nitrosobenzene undergoes electrophilic aromatic substitution (EAS) when treated with nitric acid and sulfuric acid. (This question continues on p.9 and 10.)

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 electrophile and all of the resonance structures for the key intermediates. Be sure to show all three steps in the EAS reaction.

Mechanism for para substitution:



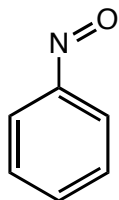
score

Long questions (Points as shown)

Name _____

13 a) (contd.)

Mechanism for meta substitution

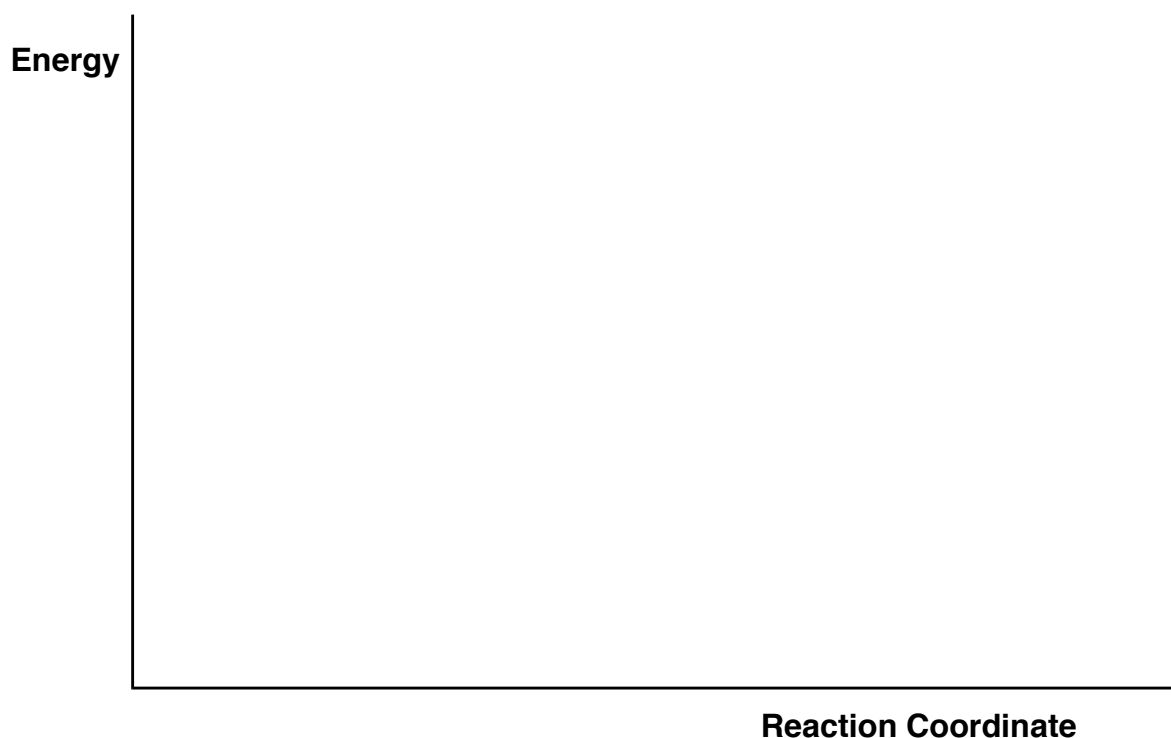


score

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.



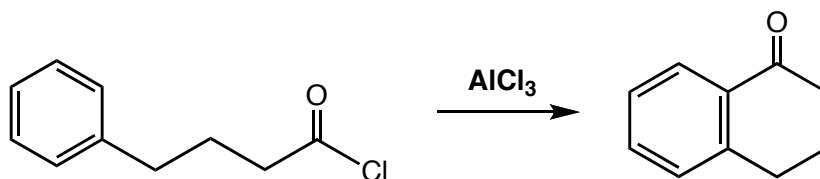
Note: No need to draw out structures - just labels such as SM, PROD, σ -COMPLEX. are fine.

score

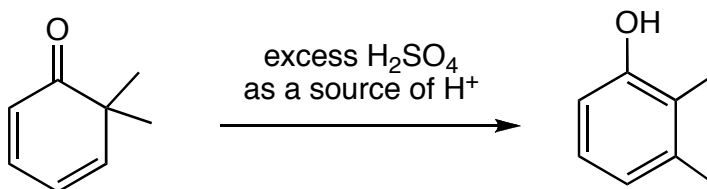
| |
|--|
| |
|--|

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

a.



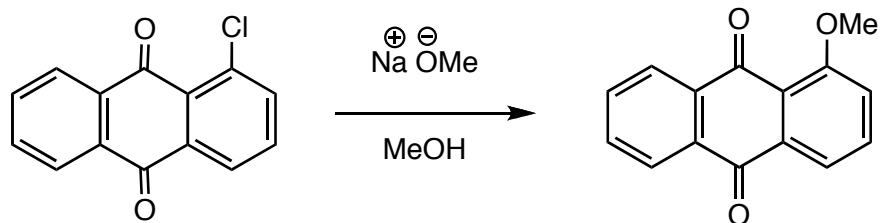
b.



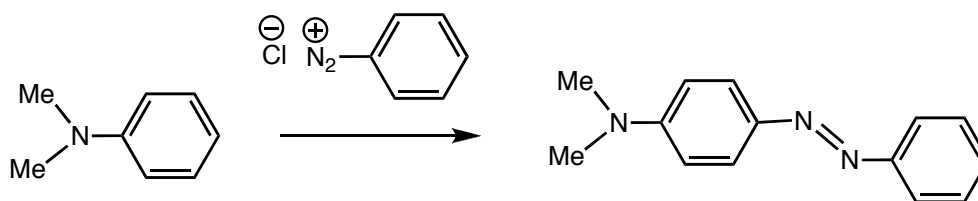
score

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

c.



d.



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

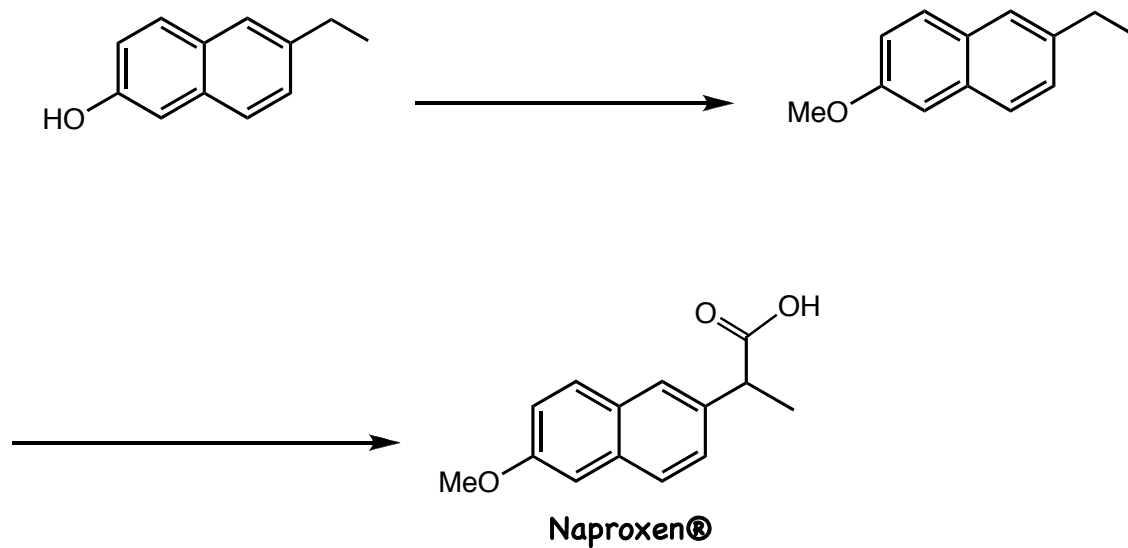
score

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!



score

<http://www.ktf-split.hr/periodni/en/>

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(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)

Relative atomic mass is shown with five significant figures. For elements having no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotopes of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

4

Editor: Aditya Vardhan (adityan@noelnix.com)

Important Electronegativity Values

| | | | | | | |
|-----------|-----------|-----------|-----------|----------|----------|-----------|
| H 2.2 | | | | | | |
| Li 1.0 | Be 1.6 | B 1.8 | C 2.5 | N 3.0 | O 3.4 | F 4.0 |
| Na 0.9 | Mg 1.3 | Al 1.6 | Si 1.9 | P 2.2 | S 2.6 | Cl 3.2 |
| K 0.8 | | | | | | Br 3.0 |
| | | | | | | I 2.7 |

BLANK FOR ROUGH WORK