

**Chemistry 547 Fall 2011
Final Examination**

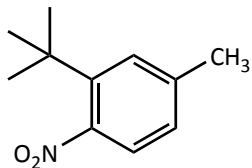
Name _____

1. (24 pts) Structure, nomenclature and stereodescriptors!

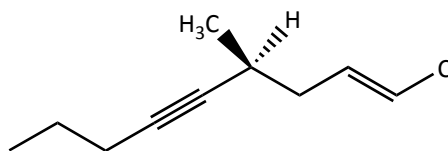
Final exams will be handed back at the beginning of next semester.

Write a complete name corresponding to each structure. Include all necessary stereodescriptors.

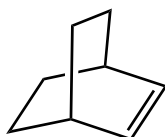
a)



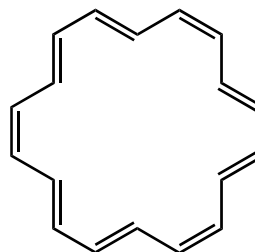
3 pts



3 pts



3 pts



3 pts

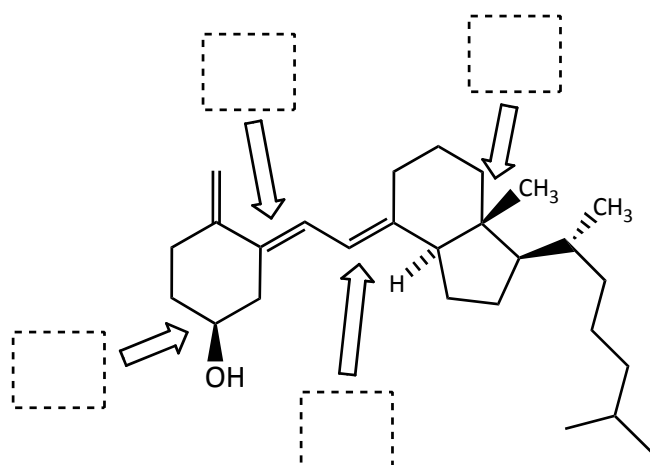
b) The structure of Vitamin D₃ is shown. This substance, which is essential for calcium absorption in humans, is produced in several steps from cholesterol.

What is the molecular formula for Vitamin D₃? _____

2 pts

Assign stereochemistry (R, S, Z, E) at each indicated stereocenter. (answers should go in the boxes)

8 pts

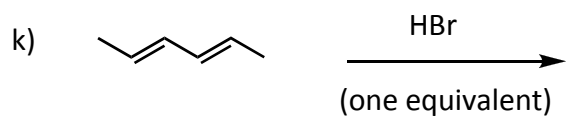
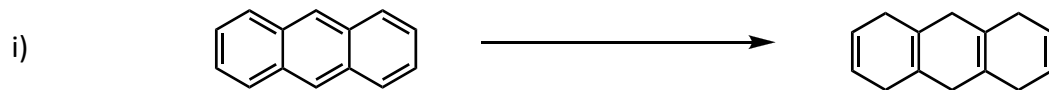
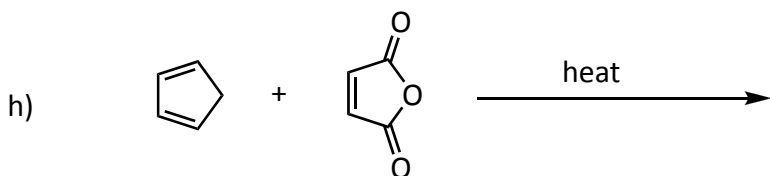
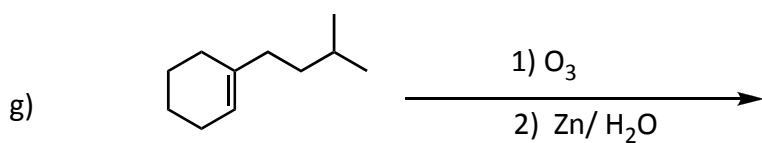
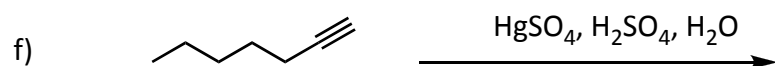
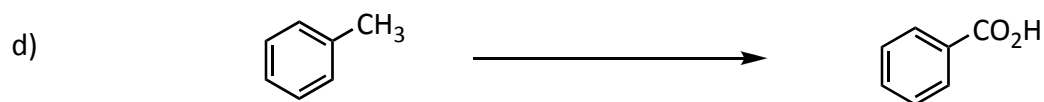
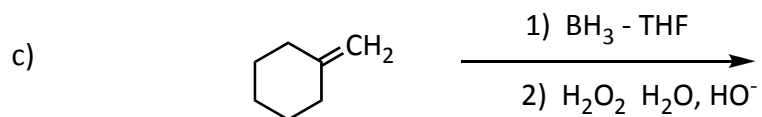
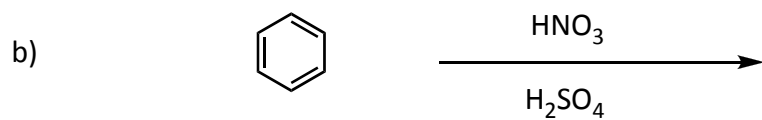
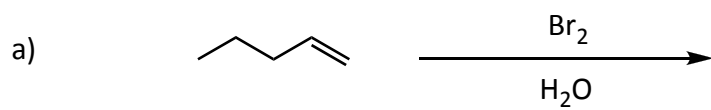


Considering *all* stereogenic centers, how many stereoisomers are possible for vitamin D₃? Explain.

2 pts

2. (30 pts) Reaction chemistry. Complete each reaction with major product(s) or necessary reagents. "NO REACTION" is NOT a possible answer.

2

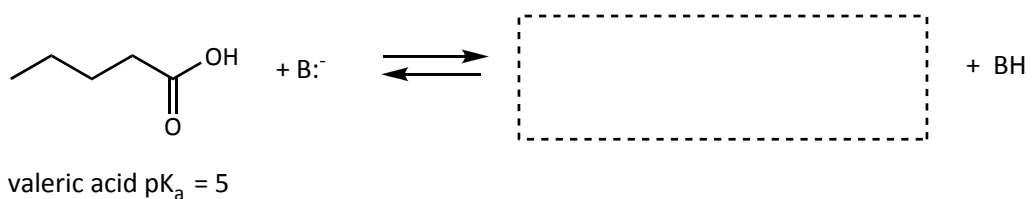
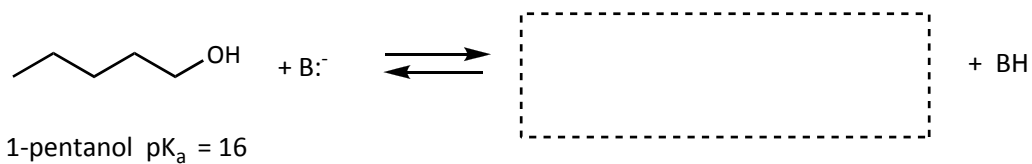


Hint: show both reaction products

3. (16 pts) Structure and bonding.

a) Valeric acid is *ca.* 1 trillion times more acidic than 1-pentanol. B^- is a generic base. Complete each equation below, showing the conjugate base of pentanol and valeric acid.

4 pts

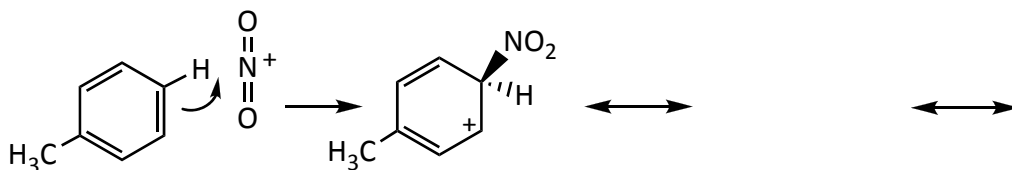


b) In a short paragraph and using any necessary structures, **explain** the dramatic *difference* in acidity of the two substances shown above.

3 pts

c) In the first step of electrophilic nitration of toluene, the nitronium ion adds to give a carbocation intermediate. **Draw** the remaining two resonance structures. **Circle the one resonance structure that is most stabilizing.**

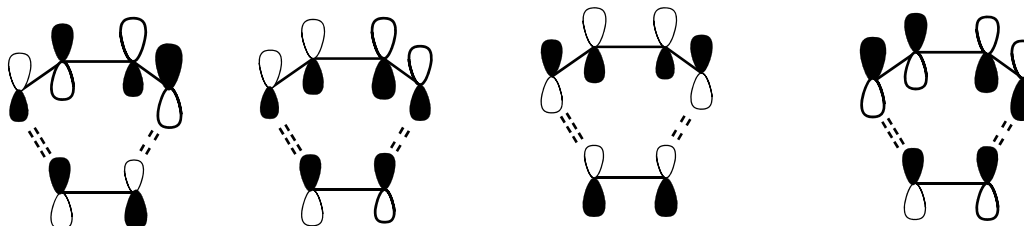
3 pts



d) **Which orbital array** correctly describes a HOMO-LUMO interaction in the Diels-Alder cycloaddition?

3 pts

circle
the best
answer



e) 3 pts Which one of the following is NOT an allotrope of carbon? (circle one answer)

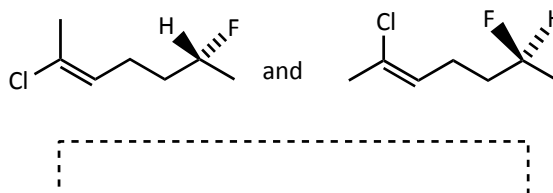
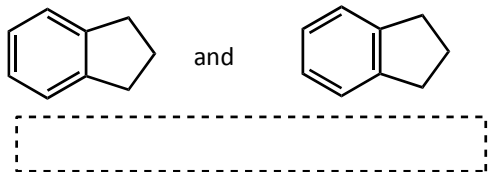
3 pts

carbon nanotubes anthracene graphite C_{60} fullerene diamond

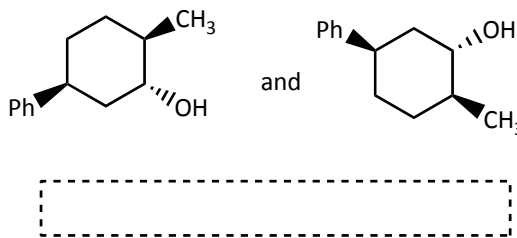
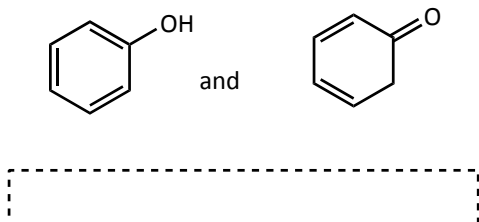
4. (14 pts) Structure, stereochemistry and conformational analysis.

4

a) Indicate the best relationship between each pair of structures below. Possible answers include, enantiomers, diastereomers, conformers, tautomers, constitutional isomers, BFF's or resonance structures.

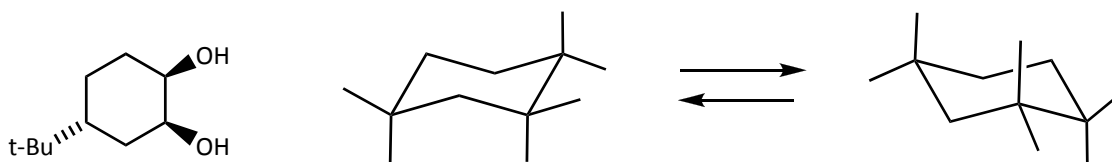


12 pts



b) Draw both chair conformers for the structure below, maintaining the correct stereochemistry and showing **which conformer is of lower energy**. Partial structures are given.

t-Bu = *tertiary-butyl*

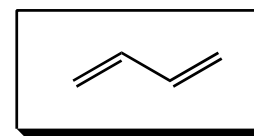
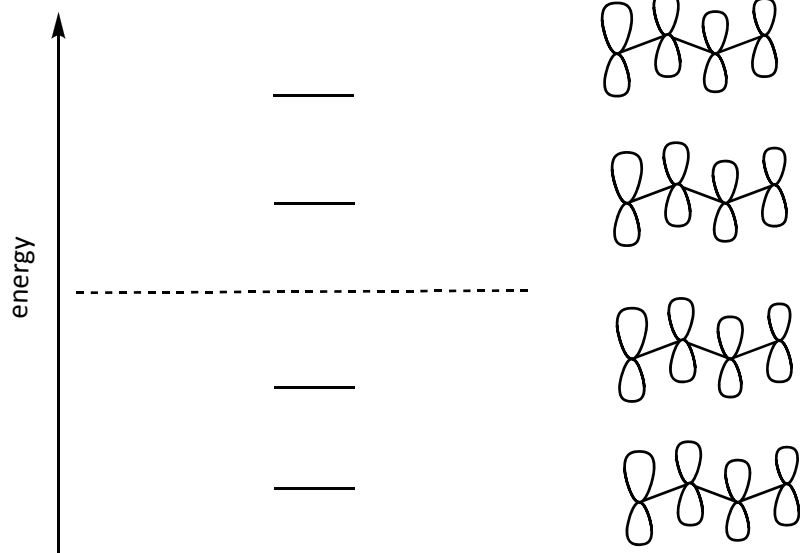


4 pts

5. (6 pts) Molecular orbital theory. Shown below is a molecular orbital energy diagram for the π molecular orbitals of 1,3-butadiene.

Complete the molecular orbitals, showing correct phases.

4 pts



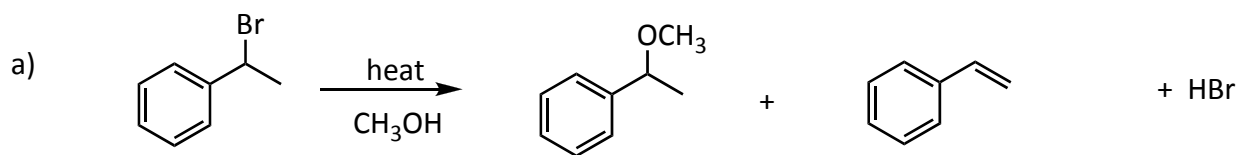
Show the **orbital occupation** for the electronic ground state of 1,3-butadiene.

2 pts

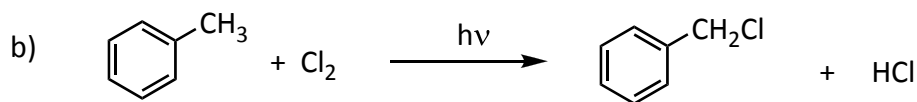
6. (24 pts) Reaction mechanisms.

5

Draw a complete mechanism for reactions a and b, complete with curved arrows to show electron "flow".



8 pts



8 pts

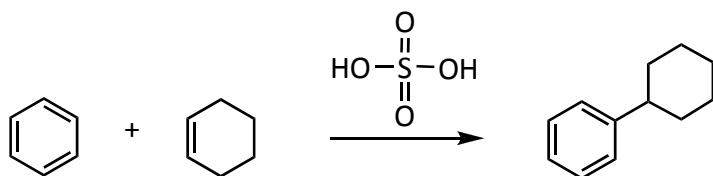
Initiation Step

Propagation Steps

Show one termination step in this mechanism.

c) Reaction of a mixture of cyclohexene and benzene with catalytic sulfuric acid gives primarily phenylcyclohexane. The most likely mechanism is electrophilic aromatic substitution. Propose a complete stepwise mechanism.

8 pts



7. (8 pts) Multistep synthesis.

Complete each two step synthesis below. Show all reagents and intermediate stages but do not draw mechanisms.



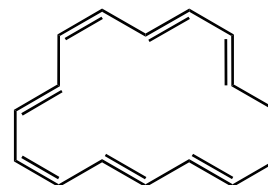
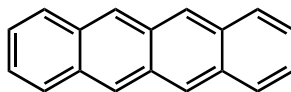
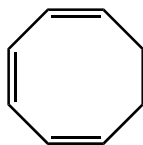
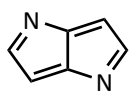
8. (14 pts) Resonance and aromaticity.

a) Briefly summarize Huckel's rule for aromaticity.

3 pts

b) Label each structure below as aromatic, antiaromatic or nonaromatic.

8 pts



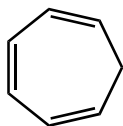
c) The acidity of cyclopentadiene and cycloheptatriene differs by a factor of 10^{20} (!!!). Using the structures of their conjugate bases and the concepts of aromaticity, explain why.

3 pts

$pK_a = 16$



$pK_a = 36$



Draw the structure or give a specific example of each of the following.

polystyrene

a reactive Diels-Alder dienophile

m-chloroperbenzoic acid

a benzylic free radical

a regioselective reaction (show reactant, reagents and product)

a stereoselective reaction (show reactant, reagents and product)

"Imagination is more important than knowledge. For knowledge is limited to all we now know and understand, while imagination embraces the entire world, and all there ever will be to know and understand."

Albert Einstein

1. _____ / 22

4. _____ / 14

7. _____ / 8

Total

2. _____ / 30

5. _____ / 8

8. _____ / 14

_____ / 150

3. _____ / 18

6. _____ / 24

9. _____ / 12

Santa Clause: Do I have permission to upload your final grade to the North Pole database so Santa can update his "naughty" or "nice" list?

YES

NO