

Chemistry 3B
Fall, 1992

Final Examination
19 December 1992

Paul A. Bartlett

Your Name: _____

PLEASE CIRCLE YOUR SECTION NUMBER/NAME OF TA

- | | | | |
|---------------------|-------------------|--------------|-------|
| 101/Matthew Marx | 301/Whitney Smith | I (40 pts) | _____ |
| 102/Bruce Ellsworth | 311/Adam Matzger | II (30 pts) | _____ |
| 111/Jim Krom | 312/Drew Thompson | III (15 pts) | _____ |
| 112/Jason Martin | 411/Stephen Mills | IV (30 pts) | _____ |
| 211/Corey Liu | 412/Sun Yeoul Lee | V (30 pts) | _____ |
| 212/Chad Peterson | 511/Traci Hopkins | VI (30 pts) | _____ |

AT THE BEGINNING:

This exam has FIFTEEN pages;
make sure that you have them all.
Please write your answers in the boxes provided.
We will only grade the answers that are in
the boxes; please do your scratch work on the
backs of the pages.

- | | |
|---------------|-------|
| VII (15 pts) | _____ |
| VIII (35 pts) | _____ |
| IX (30 pts) | _____ |
| X (20 pts) | _____ |
| XI (15 pts) | _____ |
| XII (20 pts) | _____ |
| XIII (30 pts) | _____ |
| XIV (30 pts) | _____ |
| XV (30 pts) | _____ |

Total (400 pts) _____

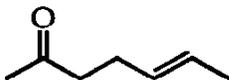
Periodic Table of the Elements

| | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

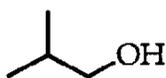
I. (40 points)

Show how to synthesize 5-hepten-2-one in an efficient manner. You do **not** have to control the stereochemistry of the double bond. The carbon atoms in your product must come from ethanol, acetaldehyde, and/or acetic acid; you may use any other reagents. Although there are many ways to do this synthesis, the best answer will include an aldol condensation and a Claisen condensation.

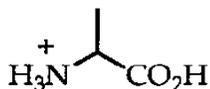


II. (30 points)

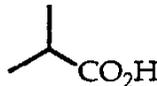
Rank the following compounds in order of decreasing acidity.



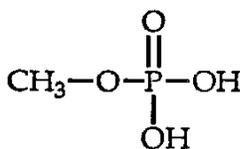
A



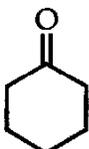
B



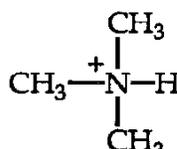
C



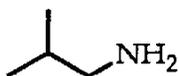
D



E



F



G



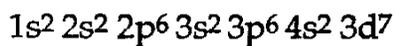
H

_____ MOST ACIDIC

_____ LEAST ACIDIC

III. (15 points)

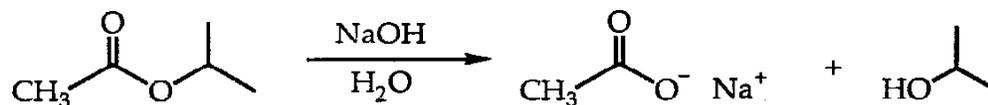
A. What element in the periodic table has the following electronic configuration?



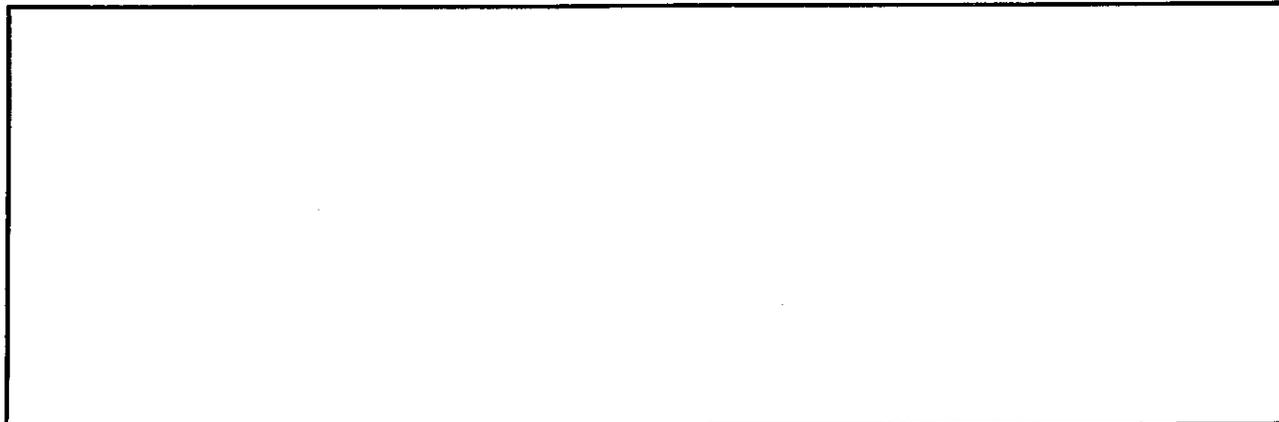
B. What is the complete description of the electronic configuration of element 43, assuming that the orbitals are filled according to the aufbau principle?

IV. (30 points)

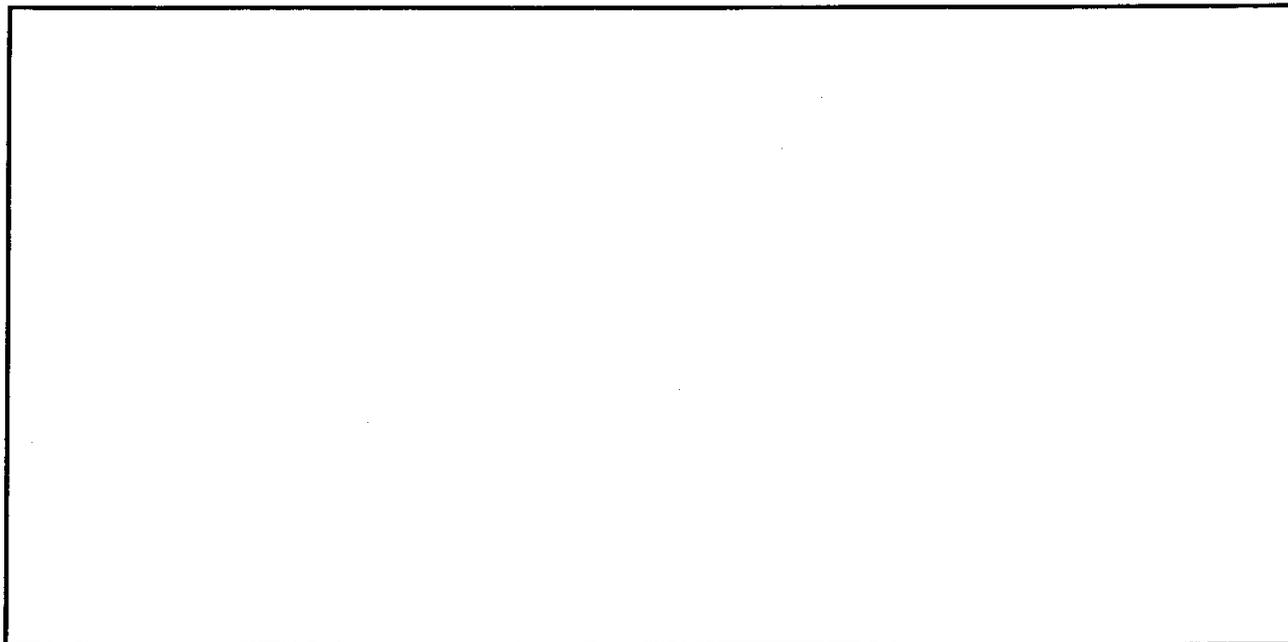
In the presence of NaOH/H₂O, isopropyl acetate is hydrolyzed to acetate and isopropyl alcohol.



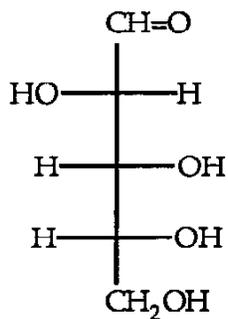
A. Show the stepwise mechanism for this reaction.



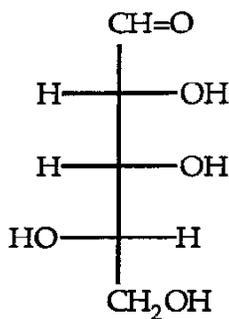
B. If the reaction is carried out in ¹⁸O-labeled water (H₂¹⁸O = "H₂●"), some of the acetate ion that is formed has **TWO** ¹⁸O atoms in it. Show the sequence of steps that accounts for this result.



V. (30 points)



D-arabinose



L-lyxose

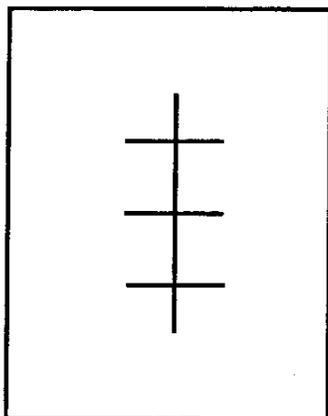
For parts A, B, and C below, the choices are: "the same", "enantiomers" or "diastereomers".

A. The two sugars above are

B. Each sugar is treated with NaBH_4 ;
the products from these reactions are

C. Each sugar is subjected to the
Ruff degradation procedure;
the products from these reactions are

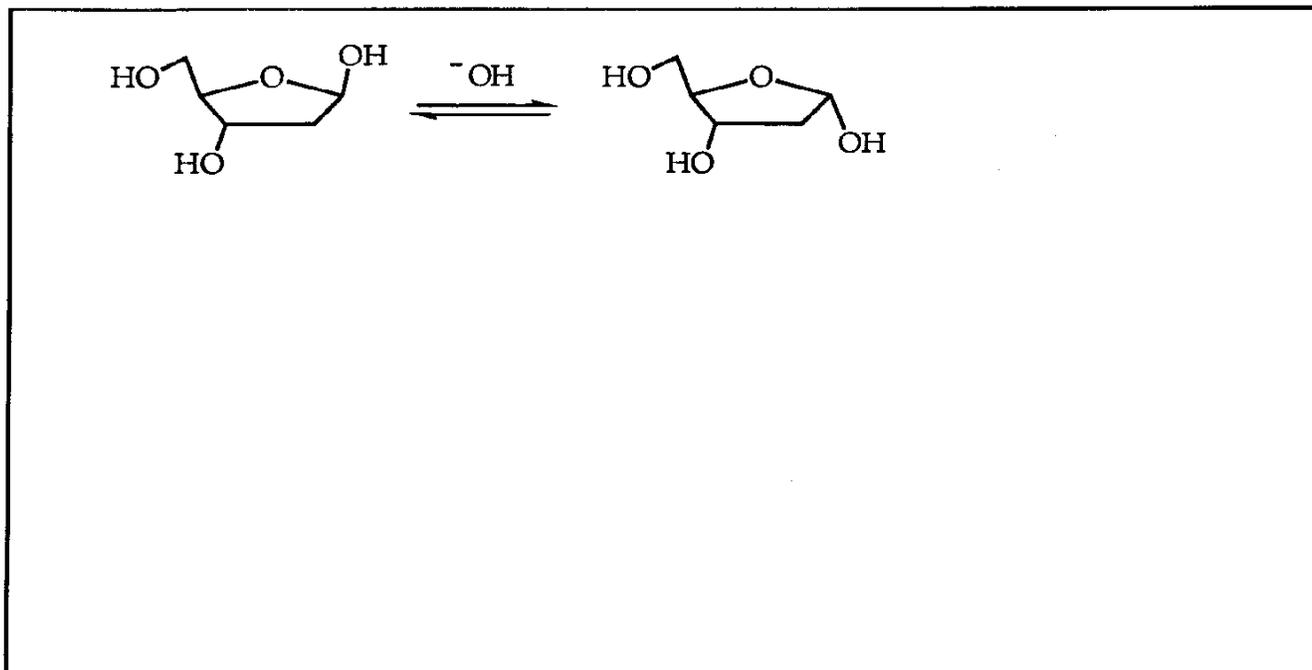
D. Write the structure of an isomeric sugar that gives the same product as D-arabinose
on Ruff degradation.



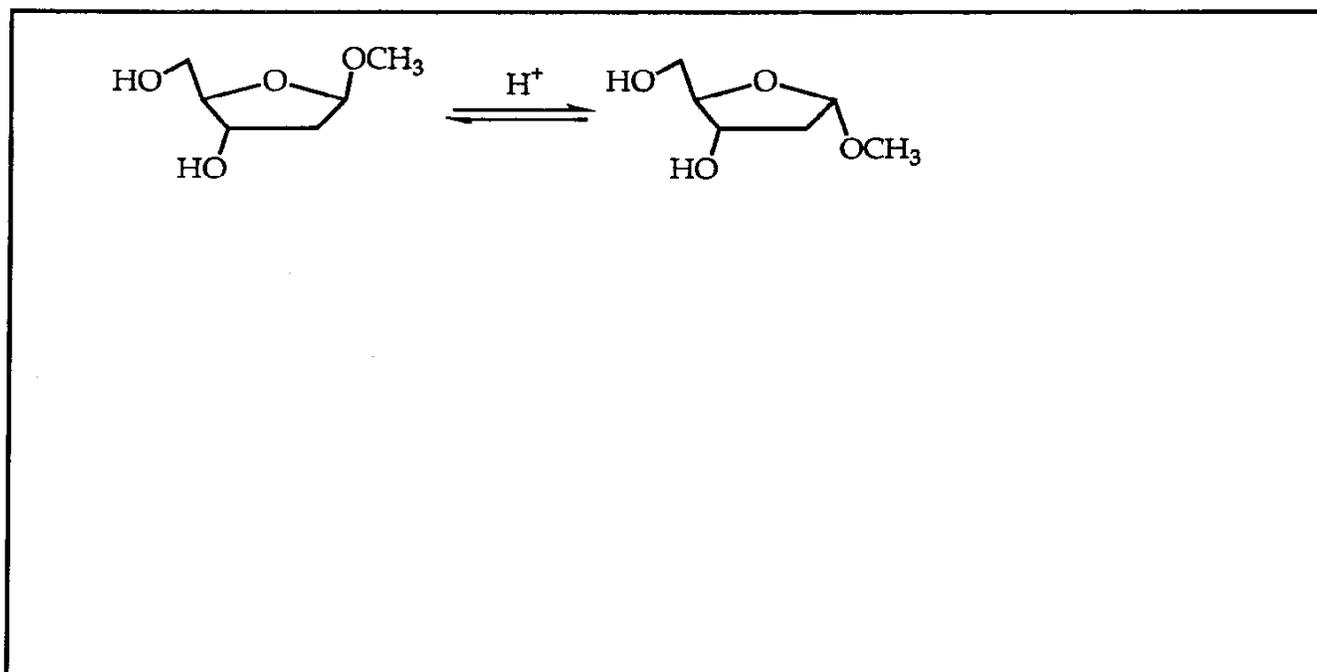
E. What is the name of this sugar?

VI. (30 points)

- A. The interconversion of the two anomers of 2-deoxyribose is accelerated by base. Write a step-wise mechanism for this isomerization.

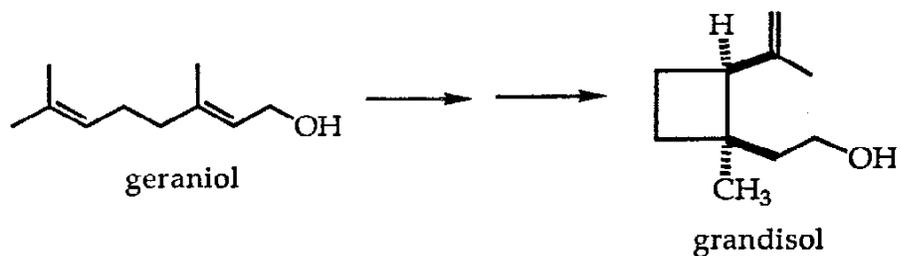


- B. The interconversion of the two anomers of methyl 2-deoxyriboside is **NOT** catalyzed by base; it requires acid instead. Show the step-wise mechanism for the acid-catalyzed isomerization.



VII. (15 points)

Grandisol, the boll weevil sex attractant, is biosynthesized from geraniol (which, in spite of its name, is a primary component of rose oil).



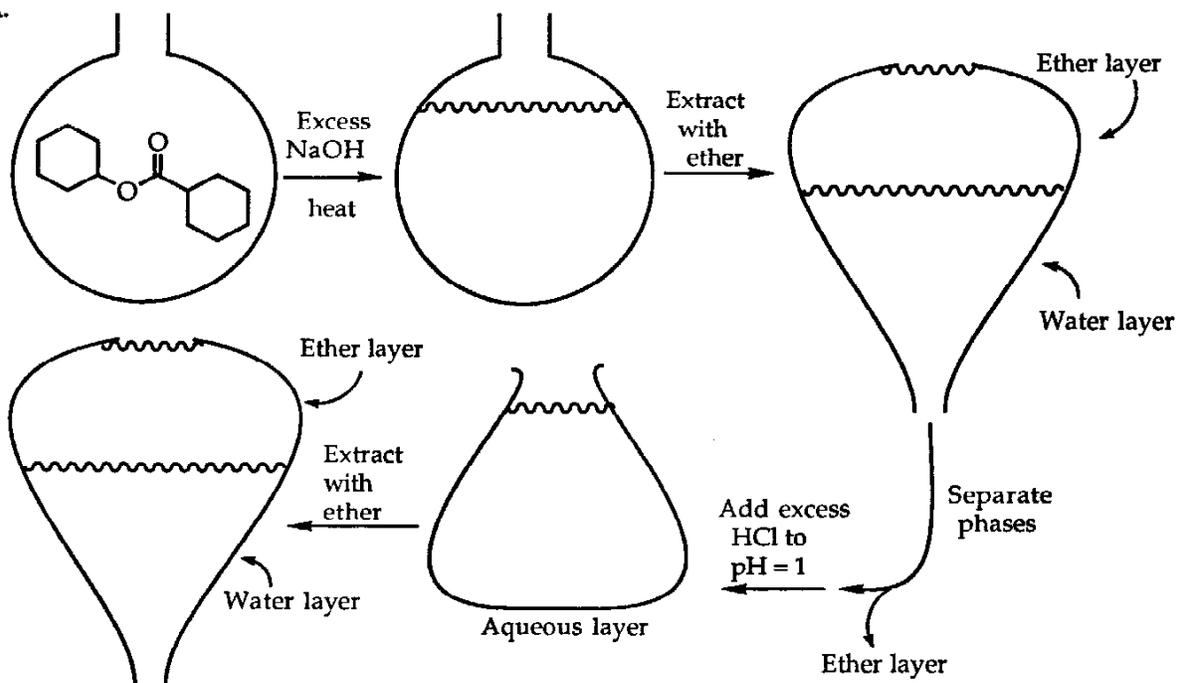
- A. Circle the isoprene units in grandisol.
- B. Write a mechanism that might account for the formation of grandisol from geraniol.

VIII. (35 points)

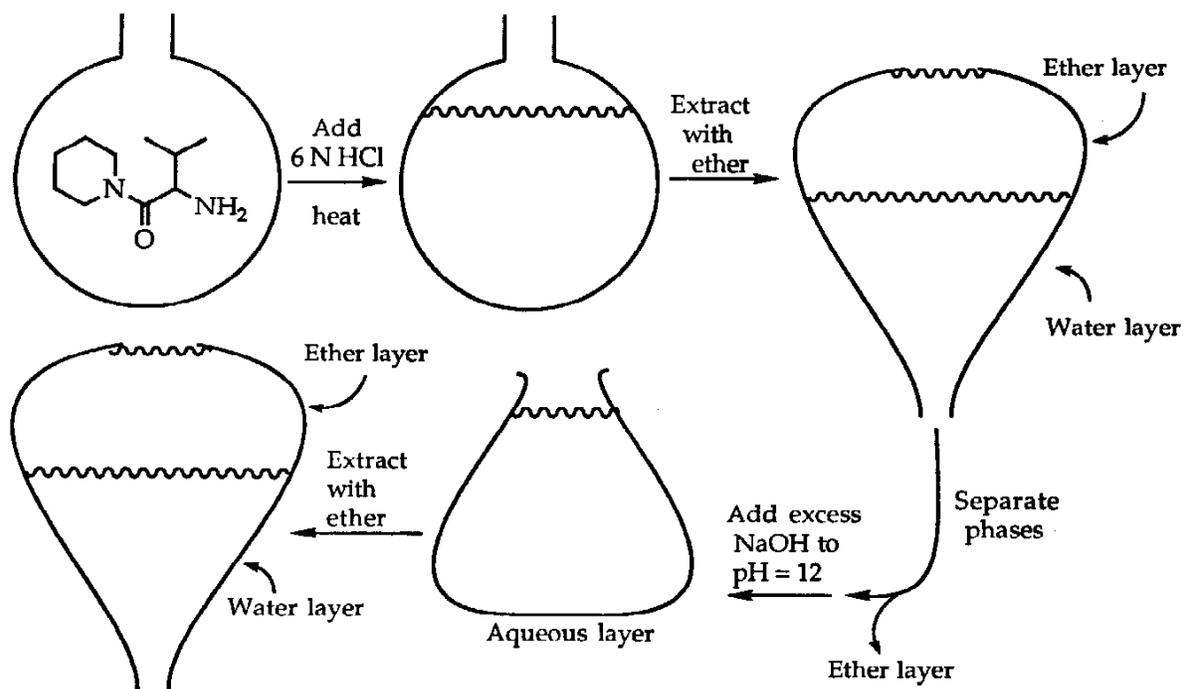
Write the structures of the organic compounds in each solution at each step of the following sequences. Pay attention to the ionization states!

If there is no organic compound in a particular solution, write "nothing".

A.

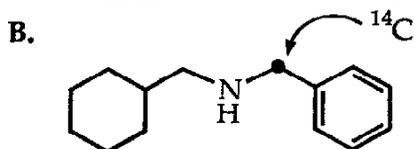
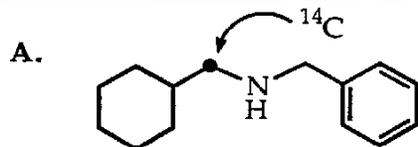


B.



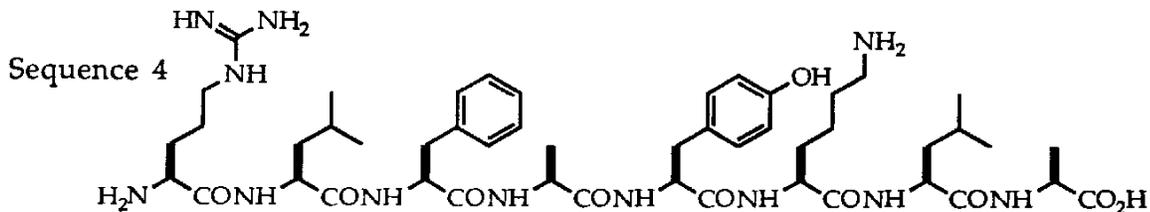
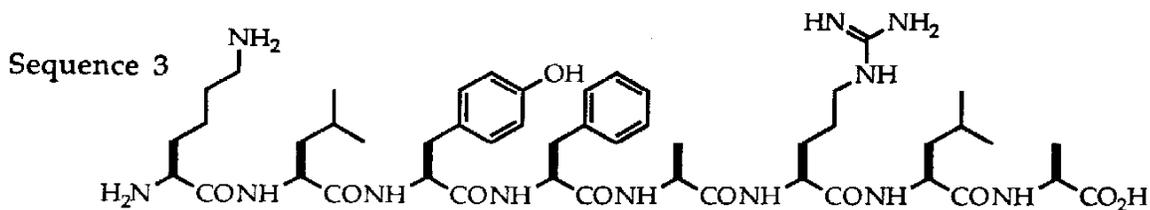
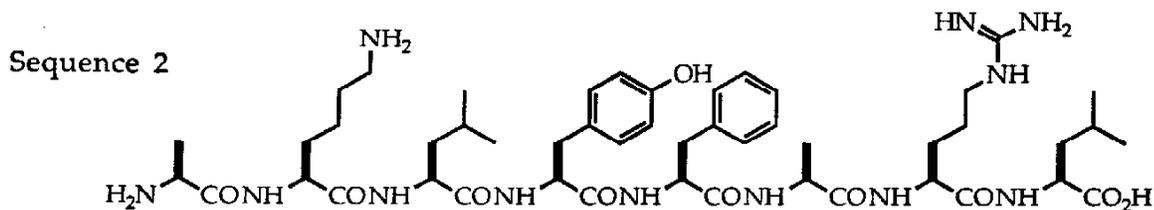
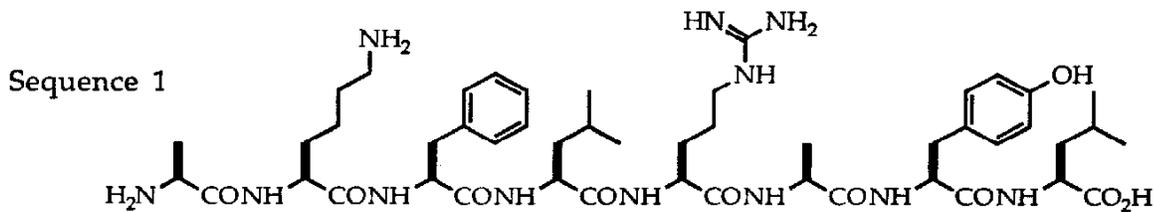
IX. (30 points)

Starting with $\text{Na } ^{14}\text{CN}$ or $\text{Na}_2 ^{14}\text{CO}_3$ ($\xrightarrow{\text{H}^+} ^{14}\text{CO}_2$) as the source of ^{14}C , along with any other reagent or starting material, show how to synthesize the following labeled amines.



X. (20 points)

An octapeptide has been isolated from the venom of a rare snake in the Amazon rainforest. The analytical instrument that Sean Connery used in "Medicine Man" is broken, but you have narrowed down the sequences to the four possibilities below.



_____ } Name the first 6 amino acids in this sequence.
 _____ }
 _____ }

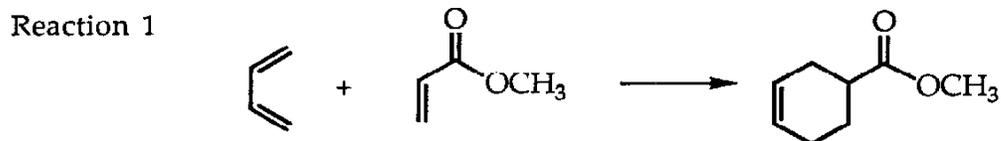
Treatment of the octapeptide with **chymotrypsin** gives a tetrapeptide, a tripeptide, and a free amino acid, while **trypsin** gives a pentapeptide, a dipeptide, and a free amino acid.

A. Which of the four sequences above is/are consistent with this information?

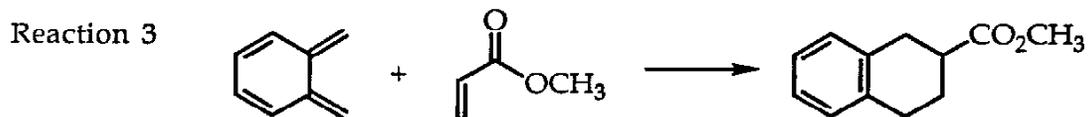
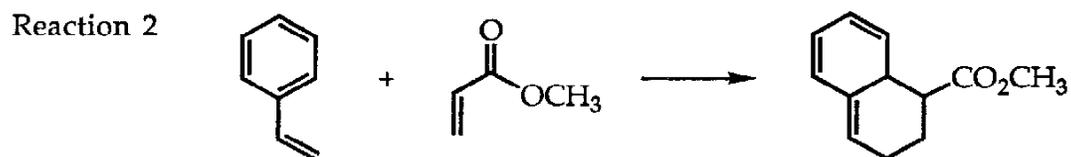
B. What test would you apply to the octapeptide to distinguish between these possibilities? Describe what reagent(s) you would use and what you would look for.

XI. (15 points)

The reaction of 1,3-butadiene with methyl acrylate (Reaction 1) is a typical example of a Diels-Alder reaction:



This reaction can also be carried out with substituted analogs of the diene component (Reactions 2 and 3).

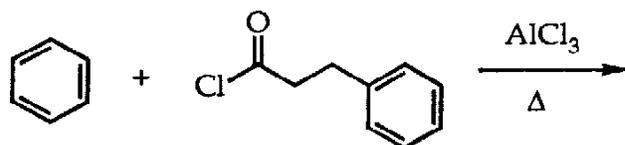


- A. Do you expect Reaction **2** to be faster or slower than Reaction 1? _____
Give a brief explanation of your choice.

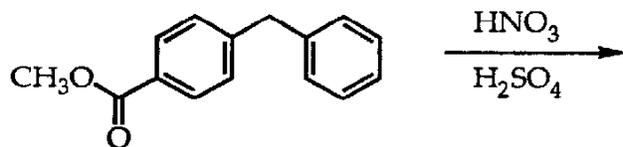
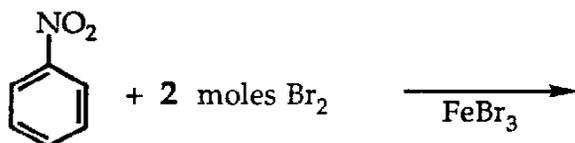
- B. Do you expect Reaction **3** to be faster or slower than Reaction 1? _____
Give a brief explanation of your choice.

XII. (20 points)

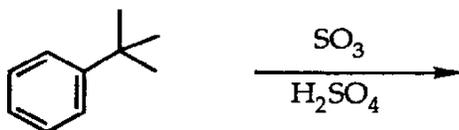
Predict the major products of each of the following reactions.



This is tricky!

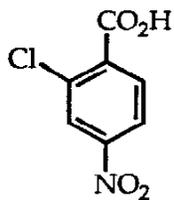
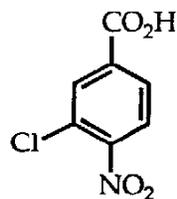
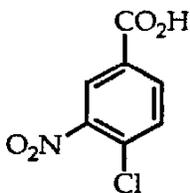
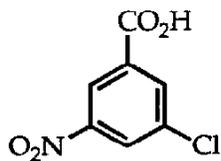


mono-nitro product



XIII. (30 points)

Show how to prepare the following compounds, using benzoic acid or toluene as starting materials.



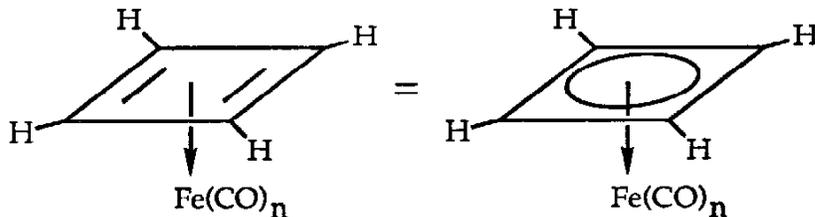
XIV. (30 points)

Predict the properties of the following compounds or elements.
Check one box for each of the four categories.

| | <- in water -> | | <- bond type -> | | <- at 25 °C, 1 atm -> | | <- color -> | |
|----------------------------------|----------------|---------------|-----------------|-------------------|-----------------------|-------|-------------|----------------------|
| | acidic | neutral basic | ionic | covalent metallic | liquid | solid | gas | none colored silvery |
| CaO | | | | | | | | |
| CH ₃ CH ₃ | | | | | | | | |
| KH | | | | | | | | |
| Pd | | | | | | | | |
| Kr | | | | | | | | |
| H ₂ PtCl ₆ | | | | | | | | |
| BaCl ₂ | | | | | | | | |
| SO ₂ | | | | | | | | |

XV. (30 points)

The isolation of the cyclobutadienyl iron carbonyl complex, depicted below, was a landmark in organometallic chemistry, since it represented the first compound with a "cyclobutadiene" group. This complex is uncharged.



- A. How many CO groups are required to fulfill the 18-electron rule? _____
 (NOTE: All the π -electrons of the cyclobutadiene complex are involved in bonding to the metal.)
- B. Several schemes can be written to account for the stable bonding arrangement in this compound. What oxidation state would you assign to the metal atom if the organic ligand (C_4H_4) has **aromatic** character? _____
- C. Justify your answer by providing an account of the electronic structure of this complex by filling in the boxes below.

| Charge on each unit | Number of electrons contributed to valence shell of metal | Contribution to the net charge of the complex |
|---|---|---|
| [Cyclobutadiene] <input style="width: 40px; height: 20px;" type="text"/> | ⇒ _____ | ⇒ _____ |
| (answer to B.) Fe <input style="width: 40px; height: 20px;" type="text"/> | ⇒ _____ | ⇒ _____ |
| (answer to A.) <input style="width: 40px; height: 20px;" type="text"/> CO <input style="width: 40px; height: 20px;" type="text"/> | ⇒ _____ | ⇒ _____ |
| | 18 | 0 |
| | Total electrons | Total charge |