Department of Chemistry
Cumulative Examinations
October 20, 2007

You may choose to answer any exam from any area covered in the examination booklet. Each exam may contain multiple parts. You may answer more than one exam but each exam is scored separately and is treated as an individual examination result. Thus, answering parts of two exams with a score of 50% *would not* yield a 100% grade for this cumulative exam. Instead you would receive 50% on each examination attempted.

This booklet contains ***four*** examinations.

On your examination booklet:

1) Print your student ID number.
2) Print this Exam Booklet number: ____________
3) Print the question number you are answering.
4) Print the Exam Date.

Do not write your name anywhere on the examination booklet. Each exam will be scored anonymously. If you attempt more than one exam, *you must use a separate examination booklet for each examination*.

When you complete the examination, return the examination and your answer booklet to the proctor. Exam results will be posted on bulletin board #2B on the north side of the hall near BRWN 2124.

PURDUE
UNIVERSITY

Analytical Chemistry Cumulative Exam
October 20, 2007
Read, and answer, all parts of all the questions.

In 1976, The Viking Mars landers used a Thermal Vaporization-GC/MS instrument in the search for soil organic matter from the surface of Mars. It did not yield a successful observation of organic carbon on Mars. 33 years later, in 2009, NASA will launch the Mars Science Lab, which will contain a very similar experiment to search for organic matter on Mars.

1. For environmental analysis, it is often the case that sampling is as important as the nature of the instrumentation used. Discuss the limitations in the Viking soil sample acquisition, and how it may have affected the results from 1976. Discuss some of the things that should be done better (and why) the next time regarding sampling, to ensure that samples containing organic carbon (if in fact they exist) are acquired.

2. In the October 1 *Analytical Chemistry* story about the performance of the previously flown TV-GCMS instrument, the article mentions, in one paragraph, that the "analytical precision", the "detection sensitivity" and the "detection limit" of the instrument were in the "ppb range". To prove conclusively that there is organic carbon in Martian soil, which of these three would be most important for your instrument, if you were to design one for this task. In your answer, define the term. For example, if you think "sensitivity" is most important, define that term, and explain why it is the key performance criterion.

3. Among the "prebiotic" molecules that the NASA team is interested in determining are long chain carboxylic acids. Describe some of the limitations of the TV-GCMS method, for fatty acid determination, and discuss how they might be overcome. Design a sampling and analysis procedure, with as much detail as you can, that might be more effective in the determination of fatty acids in Martian soils. Keep in mind the spacecraft limitations of low power, low mass, and small size. Explain how the sample would be processed, and how the sample would be input to the instrument.

4. If your objective is to simply detect organic carbon, e.g. fatty acids, explain why you might or might not benefit from a combined GC/MS method. What might the benefits/losses be of using one of these techniques alone? Explain in detail.

5. An issue for interpretation of the 1976 Viking data is the extent to which there was Fe in the soil samples, and the extent to which that Fe was Fe(III) or Fe(II). Explain exactly what the issue is with these forms of Fe, and discuss how you might avoid this problem if you were designing the experiment.

Biochemistry

1. In 1928, Frederic Griffith injected mice with a mixture of live and heat-killed S *Pneumococci* (a bacterium that causes pneumonia). In 1944, Avery et al. reported that DNA is the "transforming principle" in Griffith's experiment.

Concisely discuss why the DNA from S *Pneumococci* could cause pneumonia in mice.

2. In 1952, Alfred Hershey and Martha Chase made use of radioactive-labeled bacteriophage T2 to infect E. *coli* cells. From the results of their experiment, they concluded that DNA is "the hereditary molecule". Concisely describe the Hershey and Chase experiment and discuss how they reached that conclusion.

3. What is a cloning vector?

4. Indicate the type of sequences and features that a useful cloning vector should include. Give the reason for your answer.

5. In cloning experiments, is it preferable to have cohesive ends or blunt ends at the cloning site. Give the reason for your answer.

6. What is the difference between a genomic library and a cDNA library?

7. Suppose that you have a DNA fragment that contains a portion of the coding region for the human β–globin gene.

8. Can you use the DNA fragment as probe to screen either a human cDNA library or a human genomic DNA library? (Give the reason for your answer)

9. Suppose that you have isolated a complete cDNA and a complete piece of genomic DNA of a gene that includes 3 introns.

Do you expect that cDNA and the genomic DNA would have the same size? (Give the reason for your answer).

10. Given the sequences of both the cDNA and the genomic DNA, can you identify the introns and the exons of the gene? (Give the reason for you answer).

Inorganic Chemistry Cumulative Exam
Purdue University
October 20, 2007

Question 1: 20 points

Certain types of snake and bee venoms have very high citric acid concentrations- some over 150 mM! The exact reason for this high citric acid level is not known, but a leading theory is derived from a basic principle of inorganic chemistry. *Given that these venoms are not toxic to the snake but they are toxic to the prey*, how might you explain the high citric acid levels of these venoms? The answer is not known, so reasonable suggestions will receive credit. Citric acid is HO-C(COOH)(CH_2COOH)$_2$.

Questions 2: 20 points

A) What is the pK_a of water?
B) What is the first pK_a of $[Zn(OH_2)_6]^{2+}$?
C) What is the pK_a of water when bound to the zinc center of the enzyme carbonic anhydrase?
D) Why does the pK_a of carbonic anhydrase differ from water and $[Zn(OH_2)_6]^{2+}$?

Question 3: 20 points

You have just spent a week at sea on a research vessel, with occasional excursions in a submarine to deep sea vents 3,000 meters deep. From the samples you brought back, you have just isolated a new enzyme from a bacterium. This enzyme catalyzes the transformation of cheese curls to Twinkies. You suspect that the enzyme is a metalloenzyme. What series of experiments will you carry out to see if you have a metalloenzymes? Simply showing that the enzyme *has* a metal is only a first step. How will you prove- or disprove- that you have isolated a new metalloenzyme?

Question 4: 20 Points

Iron, copper, and zinc are quite prevalent at the active sites of many enzymes. Cobalt, on the other hand, is rare. Interestingly, many synthetic cobalt complexes exhibit favorable reactivity. Why is cobalt not found in more metalloenzyme active sites?

Question 5 (20 points)

Which of the following protein sequences will form a typical zinc finger, once Zn^{2+} is added? Explain your answer.

A) ...FACGALPEDVCWRMANLFHALWHKI...
B) ...FACGCLPEDAVWRMANLFHHKALWI...
C) ...FACGACLPELFHALWHKI...
D) ...FACGAHLPEDVWRMANLFHALWHKI...
E) ...FACGACLPEDVWRMANLFCALWHKI...
F) ...FACGACLPEDVWRMANLFHALWHKI...

PHYSICAL CHEMISTRY EXAM:
OCTOBER 20, 2007

Some useful constants to keep in mind:
hc = 1240 eV·nm
1 eV = 23.06 kcal/mol = 96.487 kJ/mol

All questions refer the paper by Yao et. al. in J. Phys. Chem. A, volume 11, page 10105.

1) (70 points) The paper describes a study of the effect of nitro- substitution on the electronic properties of iodobenzene. The properties of iodonitrobenzenes were studied by using photoelectron spectroscopy

a) Describe the experimental technique of photoelectron spectroscopy. Be sure to explain what is the physical measurement that must be made (you don't need to discuss how that measurement is made – there are a couple of ways to do it). Discuss the physical properties that are learned directly from a photoelectron spectrum. HINT: A qualitative energy diagram goes a long way in showing how it all works
b) The study is designed to investigate substituent effects. The authors discuss three ways that substitution can affect reactivity: electronically, sterically, or by solvent effects. List two ways by which a substituent can affect reactivity *electronically* (add a third for one bonus point)
c) Tables 1 – 3 of the paper list the ionization energies of o-, m-, and p- iodo-nitrobenzene.

isomer	ionization energy, eV
ortho	9.26
meta	9.35
para	9.40

The ionization energies of benzene, iodobenzene, and nitrobenzene are 9.24, 8.72, and 9.94 eV, respectively. Given this information, explain the following:
i) Why is the IE of iodobenzene lower than that of benzene?
ii) Why does the addition of a nitro-group increase the IE of iodobenzene?
iii) Why does the ortho isomer have the lowest IE of the three?
iv) (for 5 extra credit points): Why is the IE of the para isomer the highest of the three? (the authors do not address this question in the paper)

d) Given the ionization energies listed in the table above, what is the longest wavelength of light that can be used in order to carry out a photoelectron measurement on iodonitrobenzenes?
e) On page 10075 of the same issue, Leone and co-workers report a study of the VUV photoionization of small water clusters.
   a. What does VUV stand for?
   b. Discuss the difference between a photoionization measurement and photoelectron spectroscopy

2) (30 points) Photoelectron spectroscopy has been used to address many chemical questions over the years. For example, in a very famous experiment, Siggel and Thomas (J. Am. Chem. Soc. **1986**, *108*, 4360) used x-ray photoelectron spectroscopy to measure core ionization energies of carboxylic acids and carboxylate anions. To their surprise, they discovered that the core ionization energies for the oxygen atoms in the acids and the carboxylates were not very different.

A) Explain why this was a surprise
B) What was the resulting significant (earth shattering?) conclusion of their study (which isn't all that earth shattering if you really think about it – in fact, it is fairly obvious)

Periodic Classification of the Elements

I A	II A	III B	IV B	V B	VI B	VII B	VIII			I B	II B	III A	IV A	V A	VI A	VII A	0
1 H 1.00797																	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.01115	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.903	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.9044	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	57 La* 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac† (227)															

***Lanthanides**	58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
†Actinides	90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lw (257)

(Numbers in parentheses are the mass numbers of the most stable isotopes.)

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Organic Cumulative Examination
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This booklet contains *one* examination.

1) Organic Cumulative Examination, Page 1-7

Please answer on these examination pages:

1) Print your student ID number. ____________________

2) Exam Booklet number: ____________________

Do not write your name anywhere on the examination. Each exam will be scored anonymously. If you attempt more than one exam, *you must use a separate examination booklet for each examination*.

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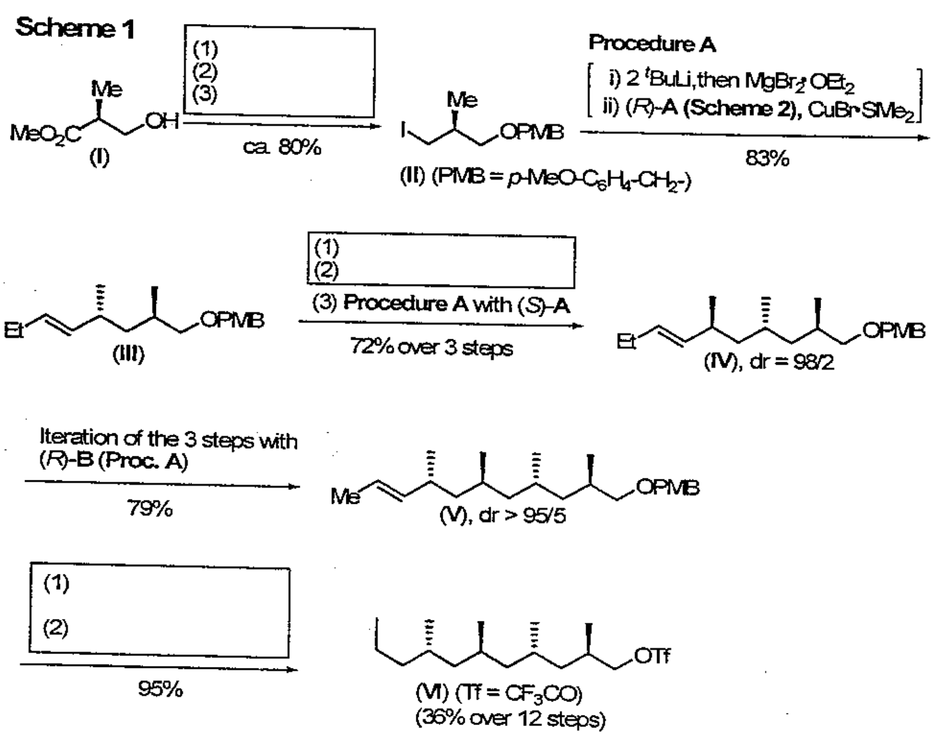
Student ID Number________________________

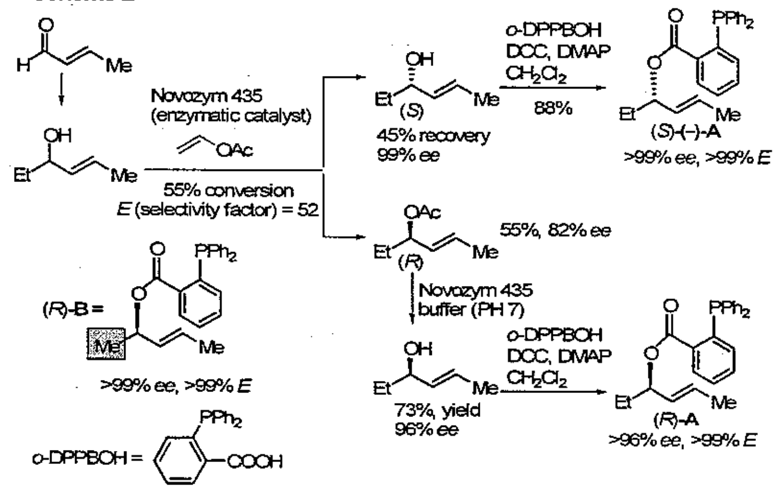
Organic Cumulative Examination

10-20-2007

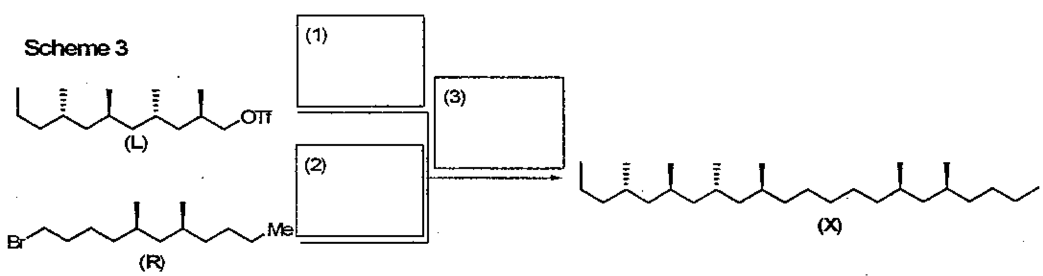
Schemes 1-3 show some details of the synthesis of 4, 6, 8, 10, 16, 18-hexamethyldocosane (*X*) by B. Breit (*ACIE* **2005**, *44*, 5267. See also *ACIE* **2004**, *43*, 3790 and a related work by K. Burgess *OL* **2007**, *8*, 1391).



Scheme 2



Scheme 3



Questions

[1] (15 pts.) How would you achieve the (**I**)-to-(**II**) conversion? Just show **appropriate reagents without using names or nature of transformation**, such as Wittig olefination or oxidation.

(1)

(2)

(3)

[2] (10 pts.) Do the same for the (**III**)-to-(**IV**) conversion.

(1)

(2)

[3] (10 pts.) Do the same for the (**V**)-to-(**VI**) conversion.

(1)

(2)

[4] (15 pts.) Judging from the results shown in **Scheme 2**, the Novozym 435-catalyzed acetylation with vinyl acetate is clearly R-selective. Why then the (S)-isomer,which was not acetylated, was obtained as an essentially pure single enantiomer of >99% *ee*, whereas the selectively acetylated (*S*)-isomer was obtained as a much less pure compound of 82% *ee*? **Your answer must be less than 50 words.**

[5] (15 pts.) Knowing the structures of (*R*)- and (*S*)-**A**, describe **very succinctly** the nature of the chain homologation steps, e.g., (*III*)-to-(*IV*), in terms of (1) stereochemistry, (2) regiochemistry, (3) possible mechanistic factor (or origin) of the observed stereochemistry.

(1)

(2)

(3)

[6] (15 pts.) The final coupling of **L** and **R** to produce (**X**) was achieved in one pot. Indicate the required reagent(s), if any, in the appropriate boxes.

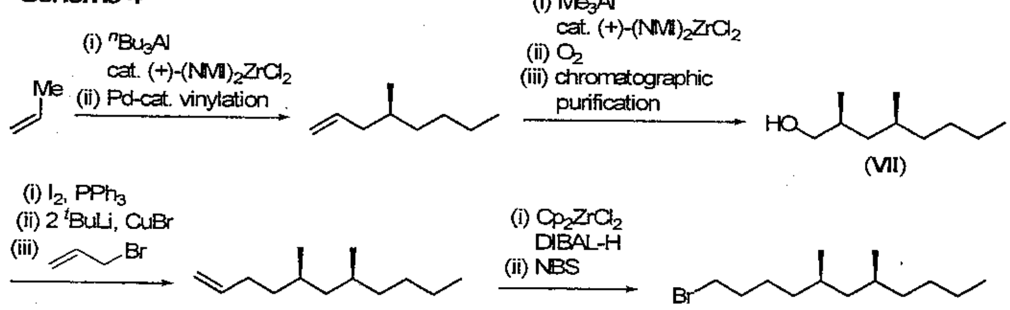
(1)

(2)

(3)

The Breit synthesis of (**R**) required 7 steps from (**I**), which must be prepared in one or more steps. Using the Zr-catalyzed asymmetric carboalumination (ZACA reaction) discovered and developed recently, however, **R** can be prepared in 4 steps (cf. *PNAS* **2004**, *101*, 5782-5787), as shown below (**Scheme 4**).

Scheme 4



[7] (10 pts.) Assuming that both of the two ZACA processes are 80% *ee* producing a mixture of the *S* and *R* isomers in a 90:10 ratio, what are:

(i) overall enantiomeric excess of (**VII**) in *ee*?

Show a brief process of calculating your answer below. Use 2 significant digits.

(ii) overall distereomeric ratio of (**VII**)?

[8] (10 pts.) Regarding stereoisomeric detection and/or purification, indicate the applicability, in principle, of the following methods. Just enter either Applicable or Not Applicable.

Method	Diastereomers	Enantiomers
• ^{1}H NMR (without added chiral reagent or solvent)		
• ^{13}C NMR (without added chiral reagent or solvent)		
• Chromatographic separation (without chiral chemicals)		
• Recrystallization		
• Enzyme-catalyzed kinetic resolution		