Chem 4B Spring 2018 Exam 3

TOTAL POINTS

80 / 100

QUESTION 1

Hydrocarbon 12 pts

1.1 name and circle stereocenters 2 / 6

+ **0 pts** Correct

cis-6-methyl-5-propylnon-3-ene

+ **1 pts** 6-methyl
+ **1 pts** 5-propyl
+ **0.5 pts** cis
+ **1 pts** non-3-ene
+ **0.5 pts** correct order (i.e. methyl propyl)

✓ **+ 3 pts correct name, incorrect backbone (takes priority over above items)**

✓ **- 1 pts wrong numbering**

+ **2 pts** 4 stereocenters (0.5 pts/ea)
+ **1 pts** 2 stereocenters
+ **0 pts** All incorrect

sec-pentyl, not isopentyl (-0.5); one stereocenter of four.

1.2 draw structure 6 / 6

✓ **+ 2 pts Cyclopentane**

✓ **+ 2 pts Correct side chains**

1-ethyl-3,3-dimethyl

✓ **+ 2 pts R stereochemistry**

+ **0 pts** all incorrect

QUESTION 2

Newman projections for hydrocarbons 18 pts

2.1 Draw skeletal structure, star same compound 12 / 12

✓ **+ 3 pts A - correct**

✓ **+ 3 pts B- - correct**

✓ **+ 3 pts C - correct**

✓ **+ 3 pts Star B & C**

+ **0 pts** all incorrect

2.2 Compound name, stereocenter? 6 / 6

✓ **+ 6 pts Correct**

3-ethyl-2-methyl-pentane

No stereocenter

+ **1 pts** 3-ethyl (if naming structure b or c)
+ **1 pts** 2-methyl (if naming structure b or c)
+ **1 pts** pentane (if naming structure b or c)
+ **1 pts** Correct order (i.e. ethyl methyl)
+ **2 pts** No stereocenter
+ **2 pts** Correct name for the wrong starred structure (2,3,3-trimethylpentane)
+ **0 pts** Incorrect

QUESTION 3

Conformations 18 pts

3.1 Stable conformation, IMF? 0 / 6

+ **3 pts** B is more stable
+ **3 pts** stabilized by hydrogen bonding

✓ **+ 0 pts Incorrect**

- 1 pts one incorrect force listed (vdW interactions, steric hindrance,...)

- 2 pts two incorrect forces listed. (vdW interactions, steric hindrance,...)

3.2 Resonance structure 0 / 6

+ **3 pts** Correct structure
+ **1.5 pts** positive charge on L carbonyl
+ **1.5 pts** negative charge on R carbonyl

✓ **+ 0 pts incorrect**

3.3 Newman projection 3 / 6

✓ **+ 3 pts correct front carbon configuration for B**

+ **3 pts** correct back carbon configuration for B
+ **1.5 pts** correct back carbon configuration for A
+ **0 pts** incorrect

QUESTION 4

4 TLC plate 12 / 12

✓ + 2 pts A (top)

✓ + 2 pts C (middle)

✓ + 2 pts B (bottom)

✓ + 3 pts All spots travel farther distance on right TLC plate

✓ + 3 pts same order as labeled in part (a)

+ 0 pts incorrect

QUESTION 5

Peptides 40 pts

5.1 Ramanchandran plot 10 / 10

✓ + 2 pts x-axis PHI, y-axis PSI

✓ + 2 pts labeled -180 to +180

cannot assume axes crossing always corresponds to (0,0)

✓ + 1 pts axes explicitly labeled degrees

OR

degree symbol on ALL number labels of axes

✓ + 2.5 pts PPI point plotted (-75, +160)

✓ + 2.5 pts RH alpha-helix region

+ 0 pts all incorrect

5.2 Helix length 7 / 7

✓ + 4 pts PPI helix would take a shorter sequence

✓ + 3 pts 1.9 Å per AA for PPI vs 1.5 Å per AA for alpha-helix

must have "1.5 Å per AA" for alpha-helix

+ 0 pts incorrect

5.3 dipeptide Pro-Pro 10 / 10

✓ + 3 pts Correct structure

✓ + 4 pts cis amide

✓ + 3 pts stereochemistry

+ 0 pts incorrect

5.4 Stabilization interaction 5 / 6

✓ + 6 pts accepted correct answers

no H-bonding in PPI

H-bonding

H-bonding in backbone

H-bonding between amine and carbonyl

+ 0 pts incorrect

H-bonding in side (R) chains

Less/reduced H-bonding

Side chain interactions

✓ - 1 pts listed 1 non-hydrogen bonding force (e.g. torsion) or geometry (e.g. cis/trans/rotation) as the reason for no H-bonding

OR any other single incorrect statement

- 2 pts listed 2 non-hydrogen bonding forces

- 3 pts listed 3 non-hydrogen bonding forces

5.5 Dihedral angle 0 / 7

+ 3 pts phi is more constrained

+ 2 pts because it is within a ring

due to R group of proline connected to N

+ 2 pts cannot freely rotate without BREAKING COVALENT BONDS

must have "bond breaking", "break bond", or equivalent in answer

no credit for "constrained", "ring strain", "steric strain", etc.

✓ + 0 pts incorrect

QUESTION 6

6 bonus question 7 / 0

✓ + 7 pts I GOT THIS

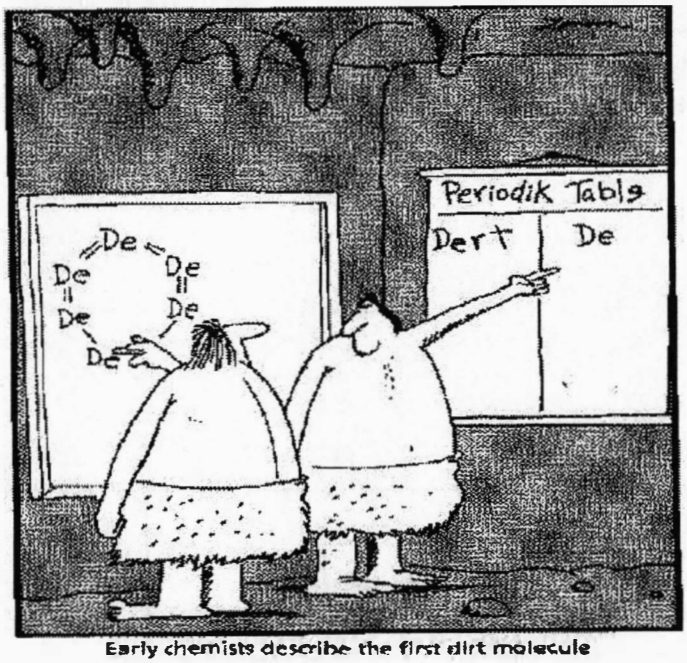
Chemistry 4B, Exam III _____

April 16, 2018 _____

Professor M.C. Hammond _____

Rules:

1. No lecture notes or books permitted
2. No calculators are needed (and are not allowed)
3. Time: 50 minutes
4. Periodic Table, Physical Constants and Conversion Factors, Structures of Amino Acids included
5. **Show all work for full credit and partial credit.**



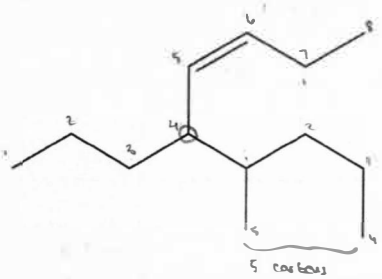
Early chemists describe the first dirt molecule

"Early chemists describe the first dirt molecule"
The Complete Far Side, 1980-1994 (Gary Larson)

BONUS (1 point): Write down the following statement below: "I GOT THIS!"

I GOT THIS!

1. a) Name the hydrocarbon shown below and circle all stereocenters, if any: (6 points)



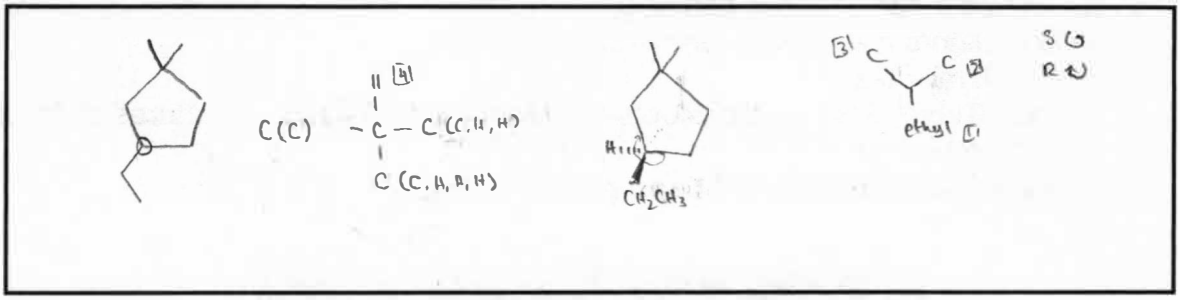
~~4-butyl-5-methyloctane X ← double bond~~

cis-~~4-pentyl-5-octene~~ ← isomer of pentane?

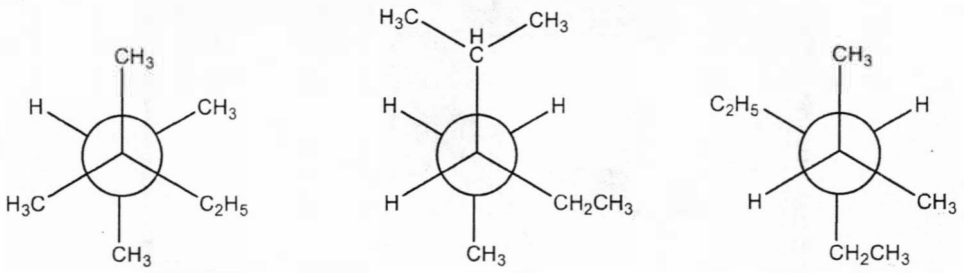
cis-4-isopentyl-5-octene

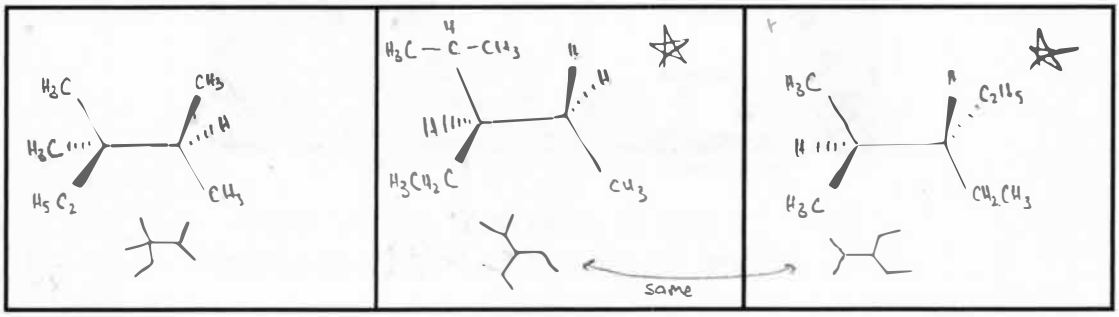
4-butyl-5-methyloctane 4-pentyl-5-octene

b) Draw the structure of (*R*)-1-ethyl-3,3,-dimethylcyclopentane. (6 points)
(*Hint: Get the structure correct for partial credit, then figure out the stereochemistry*)



2. a) Three Newman projections for hydrocarbons are shown below. Draw the skeletal structure corresponding to each structure. Star the two structures that represent the same compound. (12 points)



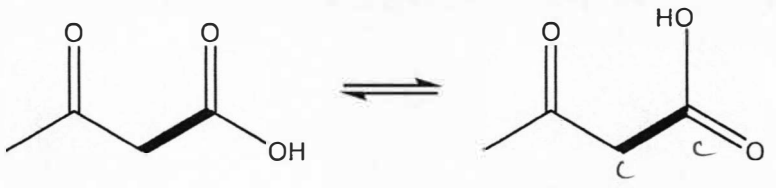


b) Name the compound represented by those two structures that you starred in (a). (4 points)

2-methyl-3-ethylpentane

c) Does it have a stereocenter? Circle: **yes** or **no** (2 points)

3. The following organic compound has two possible conformations (Note: the thicker bond is a regular single bond, but is marked for part c):



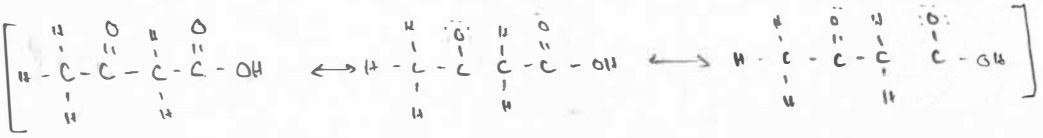
A **B**

a) Which conformation is more stable, **A** or **B**? Briefly explain what intermolecular force(s) make one conformation more stable than the other. (6 points)

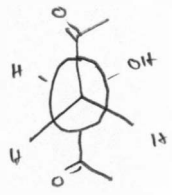
A is more stable, because there is ~~not~~ less steric repulsion with the highly polar OH group.

Hydrogen bonding / repulsion

b) Draw a resonance structure <u>that illustrates the stabilization effect</u>. (6 points)

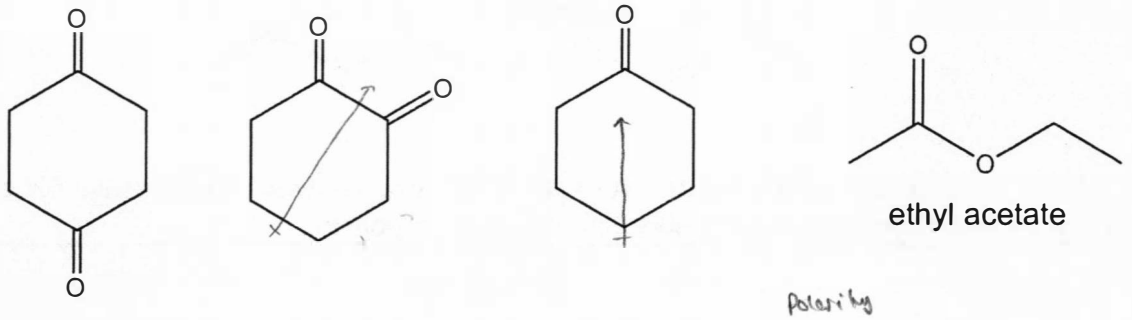


c) Draw the Newman projection for the more stable conformation along the marked C-C bond. (6 points)



4. On the left is a normal phase thin-layer chromatography (TLC) plate run using a mobile phase of 25% ethyl acetate/75% heptane to analyze a mixture containing the compounds shown.
   a) Label on the TLC which spots correspond to **A**, **B**, and **C**. (6 points)

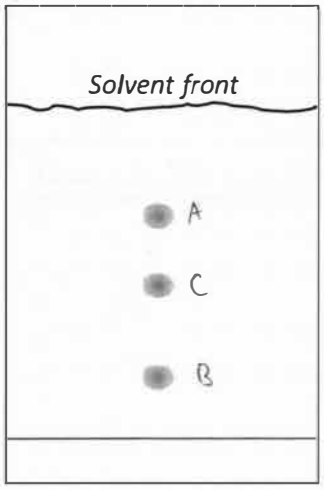
Normal: polar stationary phase

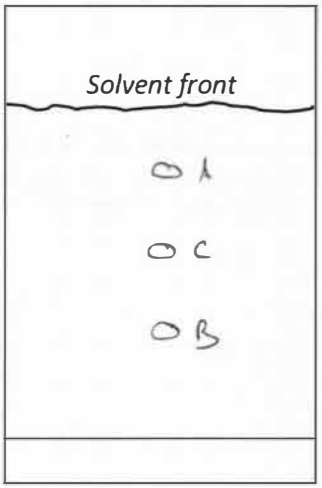


A B C

Polarity
B > C > A

Zero dipole



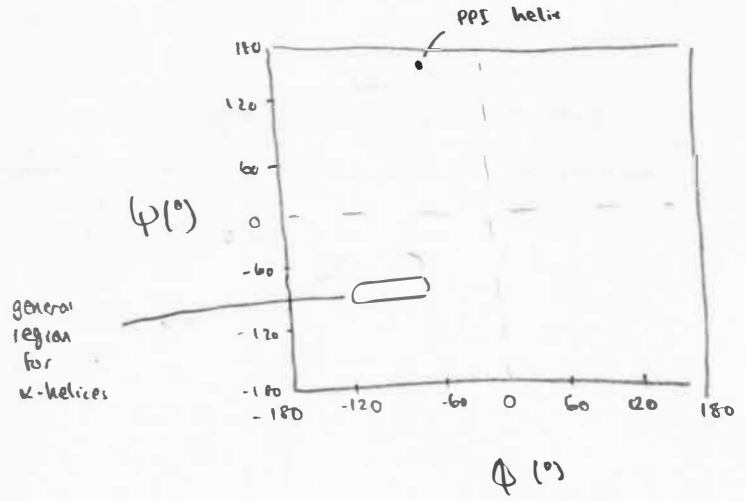


b) On the blank TLC above, draw the predicted result for analyzing the same mixture of compounds using a mobile phase of 50% ethyl acetate/50% heptane. Be sure to label the spots. (6 points)

Everything moves farther because the mobile phase more effectively competes with the stationary phase

5. Poly-Pro sequences form a unique type of secondary structure called a polyproline I (PPI) helix, which is left-handed and has dihedral angles of (Φ = -75°, Ψ = +160°).

a) Sketch a Ramachandran plot where you (i) plot the point corresponding to the dihedral angles for the PPI helix and (ii) label the general region for the regular α helix. Be sure to label your x- and y-axes. (10 points)



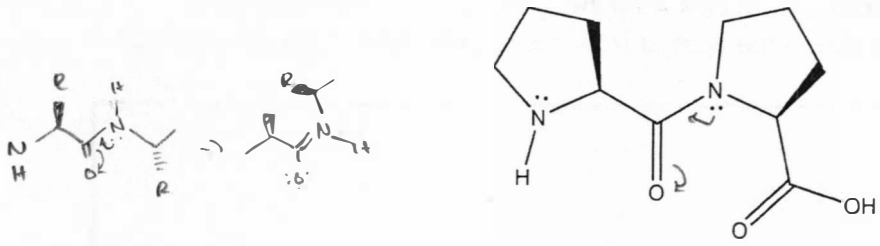
b) The rise (length per amino acid residue) for the PPI helix is 1.9 Å. Which type of helix, PPI or α helix, would take a shorter <u>primary sequence</u> to span the length of a cell membrane (~3 nm)? Explain briefly (exact calculations are **not** needed). (7 points)

α:
1.5 Å/residue

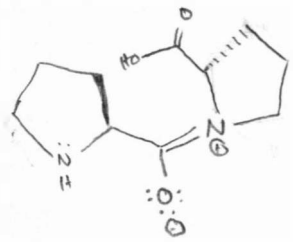
The PPI helix would take a shorter polypeptide primary sequence to span the cell membrane because an α-helix has a length of 1.5 Å per residue. Since each residue is "longer" – 1.9 Å in a PPI helix, it would take less residues which means a shorter primary sequence

Name _____

The PPI helix contains all *cis* peptide bonds. Shown is the dipeptide Pro-Pro in the *trans* configuration.



c) Draw the dipeptide Pro-Pro in the *cis* conformation, showing side chains and correct stereochemistry. (10 points)



d) Look at the structure you drew in part c. What major type of stabilizing interaction is missing in the PPI helix compared to other amino acid secondary structures? (6 points)

Hydrogen bonding in the backbone. Most helices hydrogen bond with the i+3 (3_{10}) i+4 (α) or i+5 (π) amino acid residue from the ith amino acid. However, this is not possible with the stereochemistry of the structure in c.

e) Which dihedral angle, Φ (phi) or Ψ (psi), is more constrained for Pro than other amino acids in a peptide? Explain briefly. (7 points)

Φ: NH - C_α

Ψ: C_α - CO

Ψ is more constrained for proline. As the backbone rotates around the C_α - CO bond, the proline R-group rotates around. This leads to steric repulsion between the R groups & especially the carbonyl.