

CHEM 346 – Organic Chemistry I (for Majors)

Instructor: Paul J. Bracher

Practice Hour Examination #1-2Monday, September 23rd, 2013
1:10 p.m.

Student Name (Printed)	Solutions
Student Signature	

Please also write your name on the back of the exam

Scoring

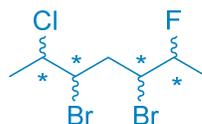
Question	Points Earned	Points Available
1		15
2		15
3		24
4		56
TOTAL		110

Original Problems, **Required Information in Answers**, and **Supplementary Explanation**

Problem 1. (15 points total, 3 points each) Determine whether the following five statements are true or false. Write out the full word “true” or “false” beside each statement; do not just write “T” or “F”. If any part of the statement is false, the entire statement is false.

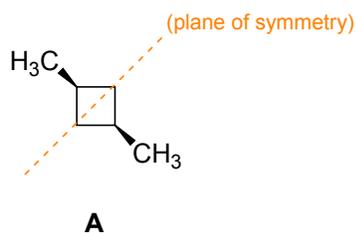
- (i) TRUE There are 16 stereoisomers of the compound 3,5-dibromo-2-chloro-6-fluoroheptane.

If you draw a Lewis structure of the compound, you will see that it has four stereogenic centers.

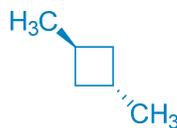


As each stereocenter can be designated either *R* or *S* (two possibilities), there are a total of $2^4 = 16$ possible permutations. The molecule also lacks a plane of symmetry that would cause some of these permutations to be equivalent.

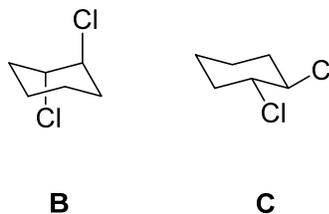
- (ii) FALSE Compound **A** has no stereoisomers, only constitutional isomers.



This compound (*cis*-1,3-dimethylcyclobutane) has an internal plane of symmetry, so it does not have an enantiomer. And while the molecule does not have any stereogenic carbons, it does have a diastereomer: *trans*-1,3-dimethylcyclobutane:



- (iii) TRUE Compounds **B** and **C** will have the same melting points and boiling points, but will rotate plane-polarized light in opposite directions.



From inspection, we can tell that both structures are 1,2-dichlorocyclohexane. For the compounds to have identical physical properties except for the direction they rotate plane-polarized light, the compounds would need to be enantiomers of each other.

The molecules are not oriented in a manner that makes determining whether they are mirror images easy. The best way to approach this determination is to assign a name to each compound. This leads us to:



These names make it obvious that the compounds are indeed enantiomers. (For a mirror image of a structure, the name stays the same except for *R*'s flipping to *S*'s and vice versa.) Enantiomers share the same physical properties but rotate light in opposite directions.

Note that while **B** is drawn with both substituents in axial positions, the compound is free to undergo conformational changes at room temperature. Both **B** and **C** will naturally form some distribution of the diaxial and diequatorial chair conformers. Drawing **B** as the diaxial Lewis structure does not imply it is “frozen” in that conformation (for the purposes of determining differences in physical properties).

- (iv) TRUE A 3:1 mixture of (*R*)-2-bromobutane and (*S*)-2-bromobutane has an enantiomeric excess (e.e.) of 50% and is optically active.

Let's just draw out 2-bromobutane to make sure it can be optically active:



Yes, the molecule does have two enantiomers. A 3:1 mixture equates to a 75%:25% mixture. Thus, the e.e. = 75% – 25% = 50%. Any excess of one enantiomer in a mixture will result in a sample with optical activity.

- (v) TRUE The *cis* isomer of 1,4-dimethylcyclohexane lies in a higher state of potential energy than the *trans* isomer.

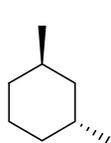
You should begin by drawing out the most stable conformation of each molecule:



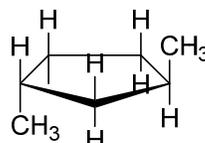
For the *trans* isomer, the two methyl groups can occupy equatorial positions, which are favorable relative to axial positions because there will be less strain in the molecule. For the *cis* isomer, in order for the methyl groups at the 1 and 4 positions to be on the same side of the ring, one methyl group must occupy an axial position. Thus, the *cis* isomer will have more strain, and thus, more potential energy relative to the *trans* isomer. You would be able to observe this difference experimentally if you subjected pure samples of both compounds to combustion calorimetry.

Problem 2. (15 points total, 5 points each) For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided.

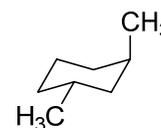
- (i) D Which of the following structures is a valid representation of (*S,S*)-1,3-dimethylcyclohexane?



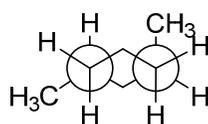
(a)



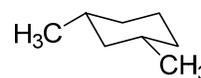
(b)



(c)



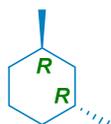
(d)



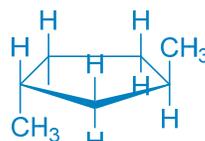
(e)

The best approach to this problem is to assign *R* and *S* designations to the stereocenters in each of these structures:

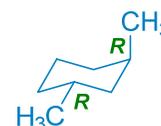
This compound has a cyclopentane ring, not a cyclohexane ring



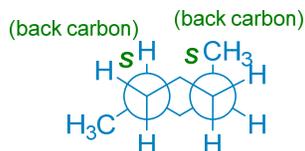
(a)



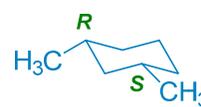
(b)



(c)



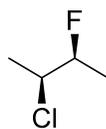
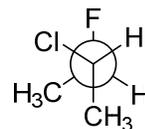
(d)



(e)

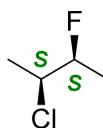
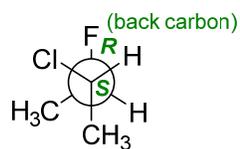
The correct answer is (d).

(ii) C The compounds represented by Lewis structure **D** and Newman projection **E** are:

**D****E**

- (a) identical compounds
- (b) enantiomers
- (c) diastereomers
- (d) constitutional isomers
- (e) conformers

The best approach to this problem is to do a quick check that the structures have the same molecular formula (they do, C_4H_8ClF) and then to name them. You can begin by assigning *R* and *S* designations to stereocenters:

**D****E**

D = (2*S*,3*S*)-2-chloro-3-fluorobutane

E = (2*S*,3*R*)-2-chloro-3-fluorobutane

The compounds have the same parent name but have mixed stereochemical designations. That means they are stereoisomers. The fact that not all of the designations are opposite means they are not enantiomers (mirror images) but diastereomers. The correct answer is (c).

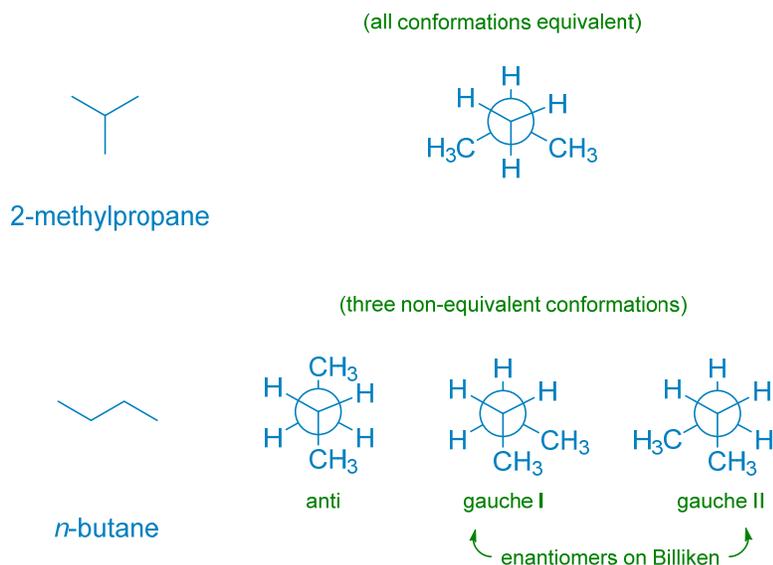
(iii) ^C

On the imaginary Planet Billiken, the ambient temperature on the surface of the planet is not high enough to provide the energy necessary for molecules to overcome the barrier to rotation between staggered conformations. How many distinct, pure isomers (including stereoisomers) with the molecular formula C_4H_{10} could you isolate on Billiken?

- (a) 2
- (b) 3
- (c) 4
- (d) 5
- (e) 6

Since conformers cannot interconvert under the conditions described, they become stereoisomers. You begin this problem by drawing out the possible constitutional isomers, then the *R* or *S* stereoisomers of each constitutional isomer, then the conformational isomers of each stereoisomer.

Mercifully, there are only two constitutional isomers: 2-methylpropane and *n*-butane. Also mercifully, neither of these isomers has any stereocenters. Conformational isomers must be constructed by “looking down” every C–C σ bond. Fortunately, the carbons bonded to three of the same group (e.g., $-CH_3$) can't contribute multiple conformers. Thus, there are no C–C bonds to analyze in 2-methylpropane and only one C–C bond to analyze in *n*-butane:



We only consider staggered conformations because they are energy minima. All of the staggered conformations of 2-methylpropane are identical/equivalent. The three conformations of *n*-butane are not equivalent. Note that the two gauche conformers are non-superposable mirror images if you cannot rotate around the C–C σ bond, so these conformers will be stereoisomers on Planet Billiken. So, in total, there are four different isomers (including stereoisomers) of C_4H_{10} on the planet.

Problem 3. (24 points total) Short answer.

(i) (6 points) Draw an isomer of C_5H_8 that your textbook would say is not a Lewis base.

Our textbook defines Lewis bases as molecules capable of donating lone pairs or π bonds into empty orbitals, so we are looking to construct a molecule with only σ bonds and no π bonds or nonbonding pairs of electrons.

Begin by figuring out the degree of unsaturation in the molecule:

$$\Omega = \frac{2 + 2 (\# \text{ of C's}) + (\# \text{ of N's}) - (\# \text{ of H's}) - (\# \text{ of X's})}{2}$$

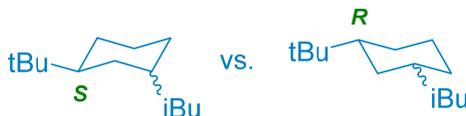
$$\Omega \text{ for } C_5H_8 = 2$$

So, we expect the molecule to have a total of two rings and π bonds. But since having π bonds would render the compound a Lewis base, our structure must have two rings. There are a limited number of ways to incorporate two rings into a structure with formula C_5H_8 , and these are the acceptable answers:

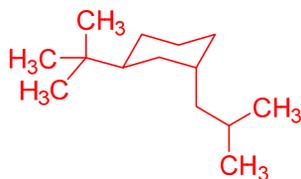


(ii) (8 points) Draw the lowest-energy chair conformation of (1*S*,3*R*)-1-*tert*-butyl-3-isobutylcyclohexane.

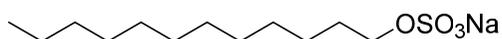
To draw the most stable chair conformation of a substituted cyclohexane, you will generally want to place the bulkiest substituents in equatorial positions to reduce strain in the molecule. When taking this approach, you must be careful to maintain all of the stereochemical relationships designated in the name of the compound. Since an axial *tert*-butyl group will generate more strain than an axial isobutyl group, let's begin by deciding in what equatorial position to place the *t*-Bu group.



Both conformations of a cyclohexane ring are drawn with a *t*-Bu group in an equatorial position and the isobutyl group drawn at the 3 position relative to the *t*-Bu group. We add the isobutyl group (with undesignated stereochemistry) to enable the assignment of *R* and *S* at the 1 position, then choose the 1*S* isomer because that is what we are told to draw by the question prompt. At this point, we simply draw in the isobutyl group such that it has the 3*R* designation also given in the question prompt. Be careful with your assignment of priorities when determining the stereochemistry at the 3 position. The isobutyl group takes priority over the back-side of the ring:

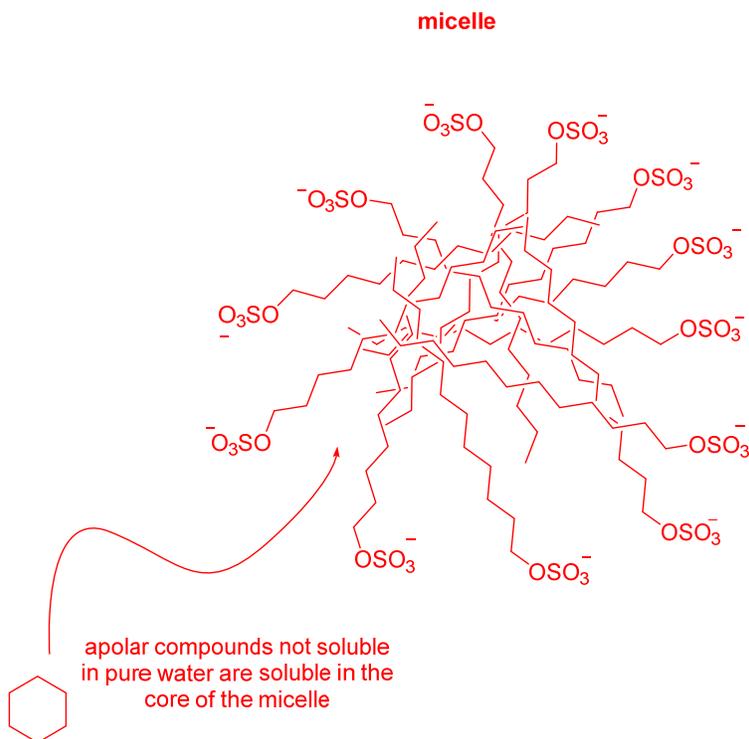


(iii) (10 points) Explain in five sentences or fewer how a surfactant like sodium dodecyl sulfate (SDS) helps improve the solubility of alkanes in aqueous media (e.g., water). Feel free to draw a picture.



sodium dodecyl sulfate

The charged head of the sulfate group on SDS gives the compound respectable solubility in water. In aqueous solution, the SDS molecules spontaneously assemble into spherical structures called micelles, where the sulfate heads interact with water molecules at the surface of the spheres and the hydrocarbon tails are oriented towards the center of the micelles. This core is an apolar microenvironment within the very polar solvent. As “like dissolves like”, relatively nonpolar hydrocarbons—which have poor solubility in water—can diffuse into the micelles where they happily interact with the hydrocarbon tails of the core.



Problem 4. (56 points total) Isomers of C_8H_{18} .

- (i) (36 points) Draw all of the constitutional isomers that have a molecular formula of C_8H_{18} . Hint: there are 18 constitutional isomers (not counting stereoisomers).

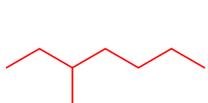
You need to develop a system. I like starting with the longest chain isomer then working down one carbon at a time. You can see a video of this method here: http://www.youtube.com/watch?v=U7GXYTFM_9I



n-octane



2-methylheptane



3-methylheptane



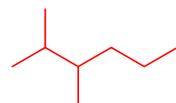
4-methylheptane



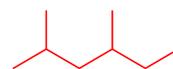
2,2-dimethylhexane



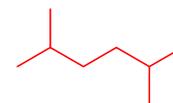
3,3-dimethylhexane



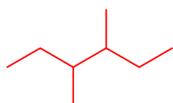
2,3-dimethylhexane



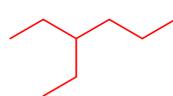
2,4-dimethylhexane



2,5-dimethylhexane



3,4-dimethylhexane



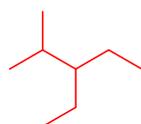
3-ethylhexane



2,2,3-trimethylpentane



2,2,4-trimethylpentane



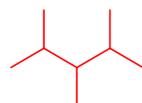
3-ethyl-2-methylpentane



2,3,3-trimethylpentane



3-ethyl-3-methylpentane



2,3,4-trimethylpentane



tetramethylbutane

(ii) (8 points) Draw the pair of enantiomers of C_8H_{18} that have both a stereocenter and a quaternary (4°) carbon. Write the name of each compound below its structure.

We can begin by identifying stereocenters (*) in the isomers drawn above:



n-octane



2-methylheptane



3-methylheptane



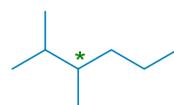
4-methylheptane



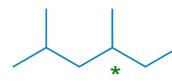
2,2-dimethylhexane



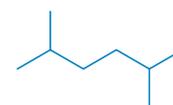
3,3-dimethylhexane



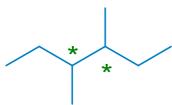
2,3-dimethylhexane



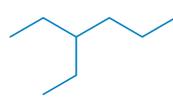
2,4-dimethylhexane



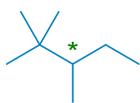
2,5-dimethylhexane



3,4-dimethylhexane



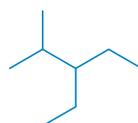
3-ethylhexane



2,2,3-trimethylpentane



2,2,4-trimethylpentane



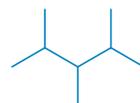
3-ethyl-2-methylpentane



2,3,3-trimethylpentane



3-ethyl-3-methylpentane



2,3,4-trimethylpentane



tetramethylbutane

Quaternary carbons are bonded to four other carbons. The only isomer of C_8H_{18} that has both a quaternary carbon and a stereocenter is 2,2,3-trimethylpentane. The two stereoisomers of the compound are the *R* and *S* enantiomers:

*(R)*-2,2,3-trimethylpentane*(S)*-2,2,3-trimethylpentane

(iii) (6 points) Identify the only stereoisomer of C_8H_{18} that is a meso compound.

In order for a molecule to be a meso compound, it has to have at least one stereogenic carbon but not be superposable with its mirror image. These conditions require at least two stereocenters with identical substituents. The only candidate from the 18 isomers drawn above is 3,4-dimethylhexane. The meso compound is the stereoisomer with one of the stereogenic carbons as *R* and the other as *S*:

*meso*-3,4-dimethylhexane

(iv) (6 points) Identify the one isomer of C_8H_{18} that is a solid at room temperature.



tetramethylbutane

If there is only one isomer that is solid at room temperature, it is going to be the one with the highest melting point. For alkanes of similar size, melting point tends to increase for structures with greater branching and more symmetry. The most branched and symmetrical isomer drawn above is tetramethylbutane. It melts at 98 °C.