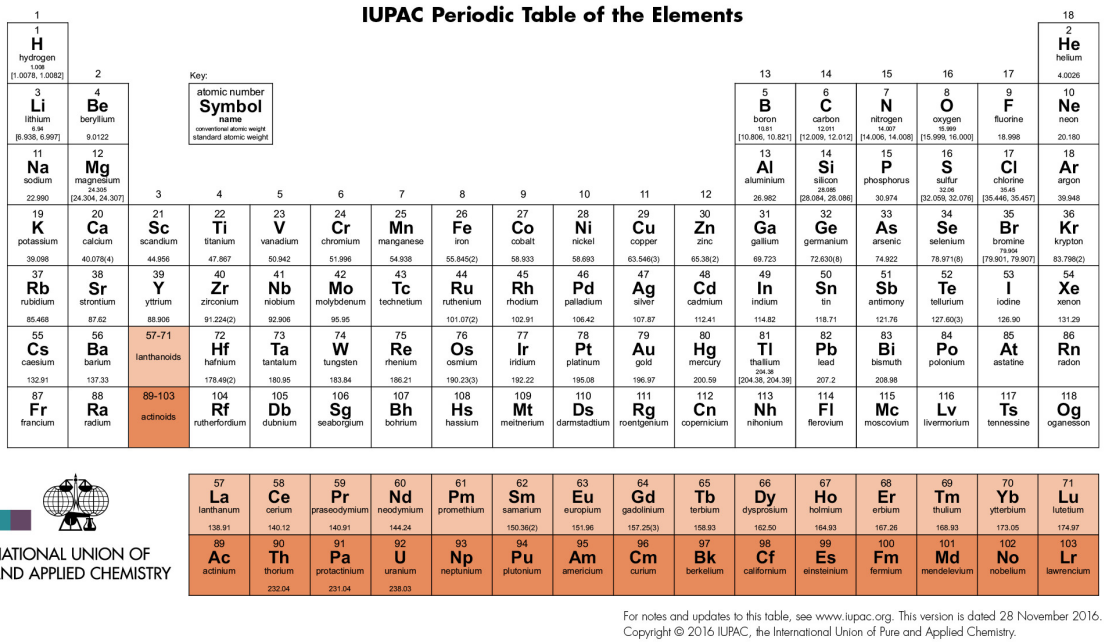
CH 334 Form A

Second Midterm Exam Monday, November 6, 2017

Name_____KEY_____

You may use model kits but no other material with chemical information without instructor approval. Tables of possibly useful data are included on the last page.

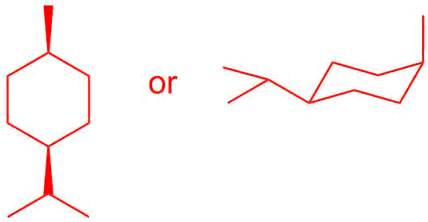
Please do not use any electronic gadgets (calculators, music players, phones, etc.).



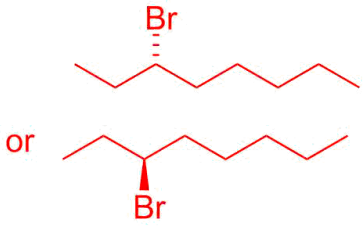
1. (15 points) Draw correct structures for the following compounds.

a. *trans*-1,3-dichlorocyclopentane

b. *cis*-4-methyl-*iso*-propylcyclohexane

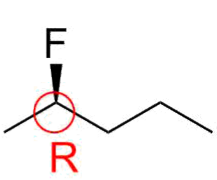


c. S-3-bromooctane

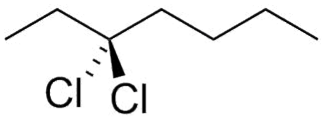


2. (20 points) Identify each molecule shown below as chiral (C) or achiral (A). Circle every stereocenter and assign the configuration as R or S.

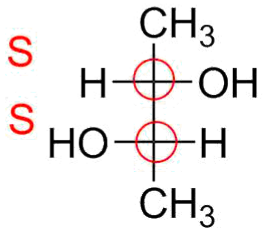
C

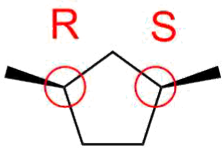


A



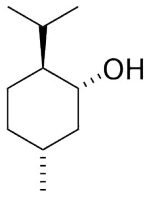
C





A (meso)

3. (20 points) Menthol, the major flavoring component in peppermint, has the following structure (right). The specific rotation, $[\alpha]_D = -50.2°$.

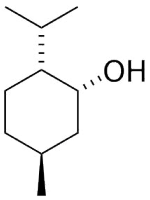


(-)-menthol

A. The enantiomer of (-)-menthol (we call it (+)-menthol) can be prepared synthetically. State what specific rotation it should show, and explain your reasoning.

It will be +50.2°. Enantiomers show equal but opposite rotations.

B. The synthesis of this enantiomer also results in a third compound, (-)neomenthol, with the structure at the right. The amount produced varies with reaction conditions but is typically 2-15%. Its specific rotation, $[\alpha]_D = -20.8°$.



(-)-neomenthol

Predict the approximate specific rotation that would be observed for the synthetic mixture of (+)-menthol and (-)-neomenthol. Explain your reasoning. (A quantitative calculation is not necessary.)

Since the rotation is opposite that of (+) menthol, the impurity would decrease the magnitude. Since the rotation would be dominated by the major isomer (there's more of it, and the specific rotation is larger), the sign would still be (+).

C. Which of the following mixtures could be separated by recrystallization (relying on different solubilities)?

-A 1:1 mixture of (+)-menthol and (-)-menthol
-A 1:1 mixture of (+)-menthol and (-)-neomenthol

Explain your choice(s) based on the nature of the stereochemical relationship between each pair of isomers.

A 1:1 mixture of (+)-menthol and (-)-menthol is a racemic mixture of enantiomers—they have the same solubilities and will be inseparable by recrystallization.

A 1:1 mixture of (+)-menthol and (-)-neomenthol is a mixture of two diastereomers. Their solubilities will differ, and at least one of these can be separated and purified by recrystallization from some solvent.

4. (25 points) This question deals with *cis*-1,3-dimethylcyclohexane.

A. Draw the two ring-flip isomers of the chair conformation of cis-1,3-dimethylcyclohexane.

B. Which of these is more stable, and by how much? Explain your reasoning.

The form on the right (diequatorial).

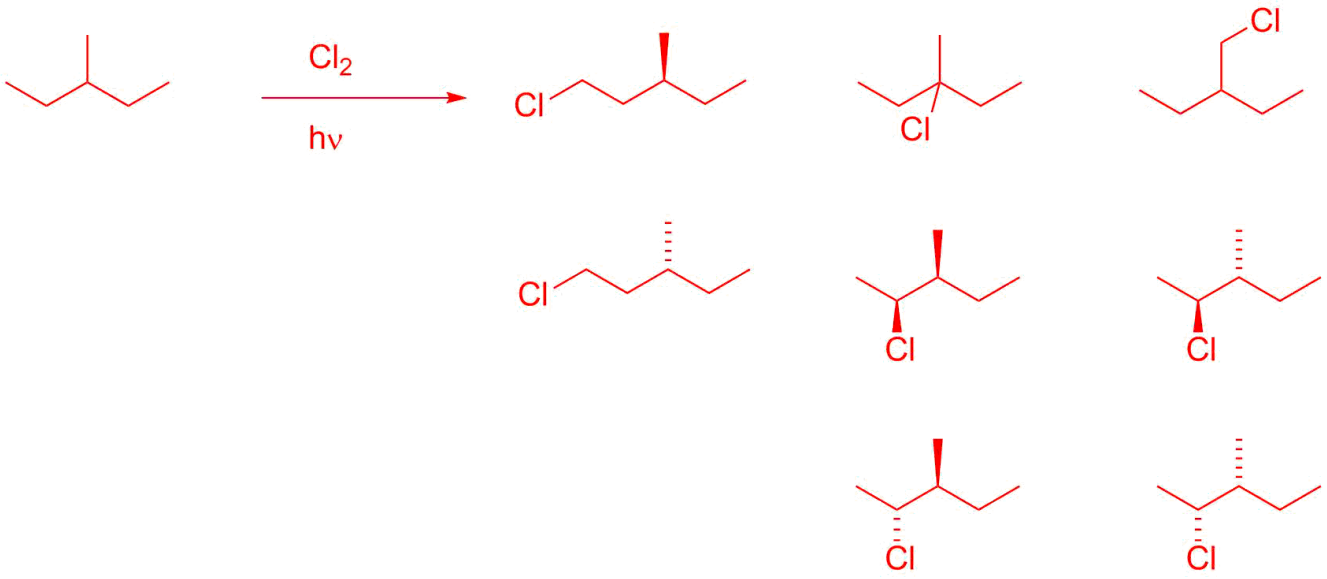
The energy cost of the diaxial form is 2 x 1.8 kcal/mol (the cost of each methyl group going axial) PLUS the cost of the methyl-methyl steric interaction (3.7 kcal/mol) = 7.3 kcal/mol.

C. How would placing an oxygen at atom 5 in the ring (in place of CH_2) change the equilibrium between the two ring flip isomers? Explain (Hint: consider why one ring flip isomer is disfavored).

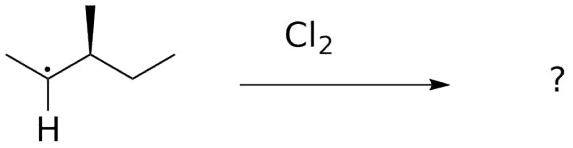
This would have a minor impact, but it does remove one 1-3 transannular interaction with an axial hydrogen in the diaxial form:

However, the transannular interaction of the methyls remains, so the cost is still > 3.7 kcal/mol. While shifting the equilibrium a little bit toward the diaxial form, the difference would be small.

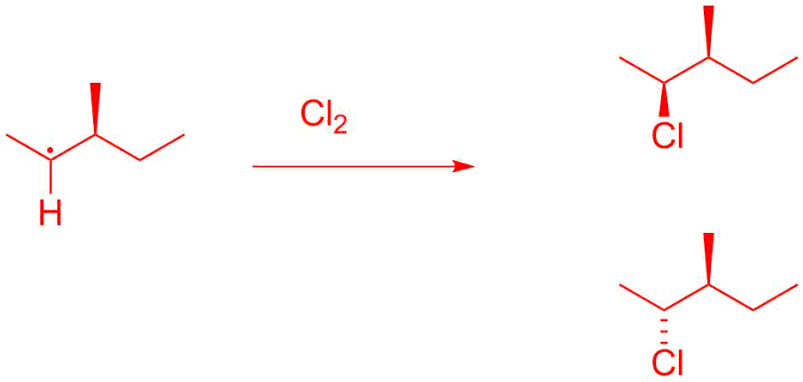
5. (20 points) Draw each product expected from monochlorination of 3-methylpentane using Cl_2 and hν. Include all distinct stereoisomers.



If the following free radical intermediate could be generated selectively (a challenging task!), would its reaction with Cl_2 generate a racemic or a nonracemic mixture of products? Explain.



The reaction would form two diastereomers: the stereocenter at C3 would be the same in both (and would be S), but formation of a new C-Cl bond can occur from either face and would create approximately equal amounts of the R and S configurations.



Bond strengths (kcal/mol):

F-F	38
Cl-Cl	58
Br-Br	46
I-I	36
H-F	136
H-Cl	103
H-Br	87
H-I	71
CH_3-H	105
CH_3CH_2-H	101
$(CH_3)_2CH$-H	98.5
$(CH_3)_3C$-H	96.5
CH_3-F	110
CH_3-Cl	85
CH_3-Br	70
CH_3-I	57
CH_3CH_2-F	111
CH_3CH_2-Cl	84
CH_3CH_2-Br	70
CH_3CH_2-I	56
$(CH_3)_2CH$-F	111
$(CH_3)_2CH$-Cl	84
$(CH_3)_2CH$-Br	71
$(CH_3)_2CH$-I	56
$(CH_3)_3C$-F	110
$(CH_3)_3C$-Cl	85
$(CH_3)_3C$-Br	71
$(CH_3)_3C$-I	55

A values (kcal/mol)

Substituent	A
Me	1.8
Et	1.8
^{i}Pr	2.1
^{t}Bu	4.5
O-Me	0.75
Cl	0.52
Br	0.55
I	0.46
Methyl-Methyl 1,3 interaction	3.7