Concordia University CHEM 221
Dr. C. Rogers, Section 02 Fall 2003

Rogers

Name: marking scheme

ID #: (answer key)

ORGANIC CHEMISTRY I -- W2005 section02

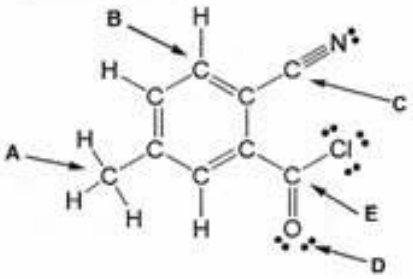
Sample MIDTERM TEST (questions mostly from F2003 MT#1&2)

↳ It's a bit too long! (1 page less is likely)

INSTRUCTIONS: This test paper includes 7 pages, 12 questions and a periodic table; check that your paper is complete. Answer all questions inside the boxes provided (except questions 11b & 12); information written elsewhere will not be marked. Model kits are allowed. **GOOD LUCK!**

#1. **(2 Marks)** What is the expected hybridization for each of the indicated atoms in this molecule?

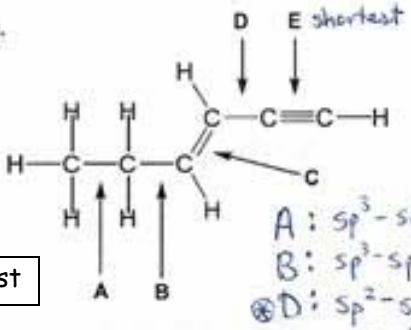
ANSWERS
A: sp^3
B: sp^2
C: sp
D: sp^2
E: sp^2



 # 2. **(2 Marks)** Rank the bonds in terms of length for this molecule.

a) longest **D > B > A > C > E** shortest
b) longest **E > C > A > B > D** shortest ✗
c) longest **A > B > D > C > E** shortest
d) longest **E > C > D > B > A** shortest ✗
e) longest **A > D > B > E > C** shortest ✗

ANSWER: **C** (not A!)

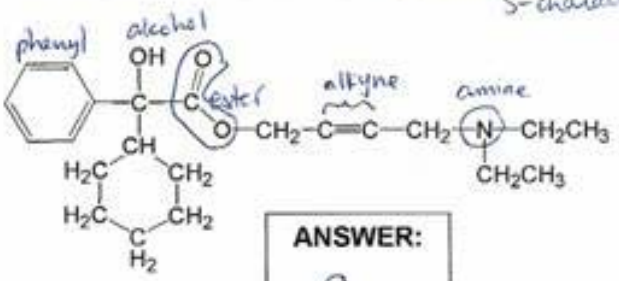


A: sp^3-sp^3
B: sp^3-sp^2
⊛D: sp^2-sp most s-character.

Of the single bonds: bond with highest s-character is shortest

 # 3. **(2 Marks)** The molecule shown here is oxybutynin, an anticholinergic compound. Which choice represents the list of functional group classes in oxybutynin?

a) ✗ (2 phenyl rings, an amine, an ester, an alkyne, a nitrile → C≡N (not present)) (only 1)
b) ✗ a nitrile, a ketone, an alcohol, a phenyl ring, an amine
c) an alkyne, an ester, a phenyl ring, an amine, an alcohol
d) ✗ an acid, an alcohol, a nitrile, an alkyne, 2 phenyl rings
e) a phenyl ring, an amine, an alkyne, a ketone, an ether ✗



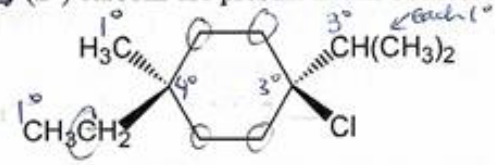
ANSWER: C

CHEM 221 Fall 2003 Section 02 MIDTERM #1-A Name: answer key

 # 4. (2 Marks) How many secondary (2°) carbons are present in this structure?

C bonded to 2 other C's

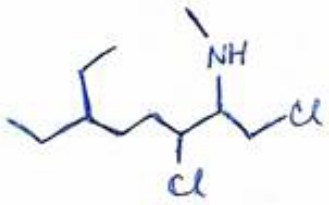
ANSWER: 5 (circled)



not Lewis, not condensed, not Kekulé!

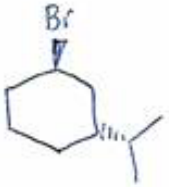
 # 5. (4 Marks) Draw line structures (= skeletal) for the following compounds:

a) *N*-methyl-1,3-dichloro-6-ethyl-2-octamine



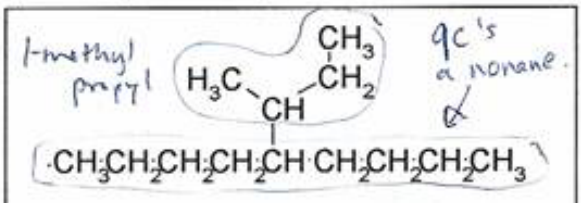
b) *trans*-1-bromo-3-(1-methylethyl)cyclohexane

Note: could instead have Br down & isopropyl up (absolute configuration not specified!)



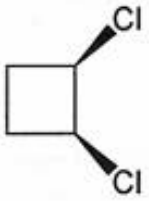
 # 6. (4 Marks) Provide systematic IUPAC names for the following compounds:

a)



5-(1-methylpropyl)nonane

b)



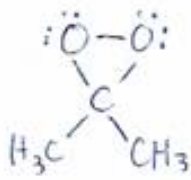
cis-1,2-dichlorocyclobutane

CHEM 221 Fall 2003 Section 02 MIDTERM #1-A Name: answer key

 # 7. (6 Marks) There are many constitutional (structural) isomers with the molecular formula $C_3H_6O_2$.

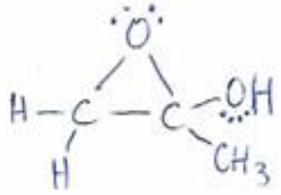
a) In each box, draw one isomer that meets the criteria listed in that box (there are a number of correct possibilities). All atoms should be closed shell (full valence) and uncharged. ie: no formal charges at all

ISOMER A: one 3-atom ring; **both** oxygen atoms are part of the ring of atoms

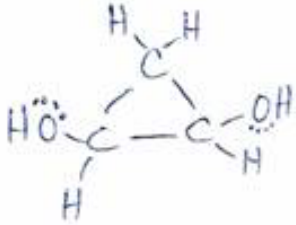


least polar

ISOMER B: one 3-atom ring; a **single** oxygen atom is part of the ring of atoms



ISOMER C: one 3-atom ring; oxygen atoms are **not** part of the ring of atoms



most polar

b) Based on the structures of the molecules, you should be able to confidently predict one of these isomers as being either the most or the least soluble in water. Choose which one you are going to identify, then explain your reasoning.

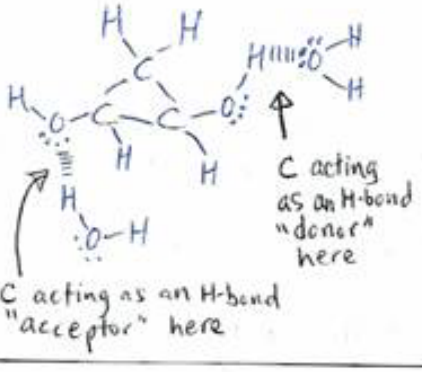
I will identify the: (circle one)

(most soluble in water (most polar)) least soluble in water (least polar)

Circle which isomer it is: A B (C)

Explanation (include sketches of relevant intermolecular interactions):

Isomer C has 2 hydroxyl groups, which can participate in hydrogen bonding with water in both "H-bond acceptor" (by sharing lone pair) and "H-bond donor" (by "donating" $\delta+$ H) modes. Thus, there will be very favourable intermolecular attractions between "C" and H_2O, which will make it dissolve easily.

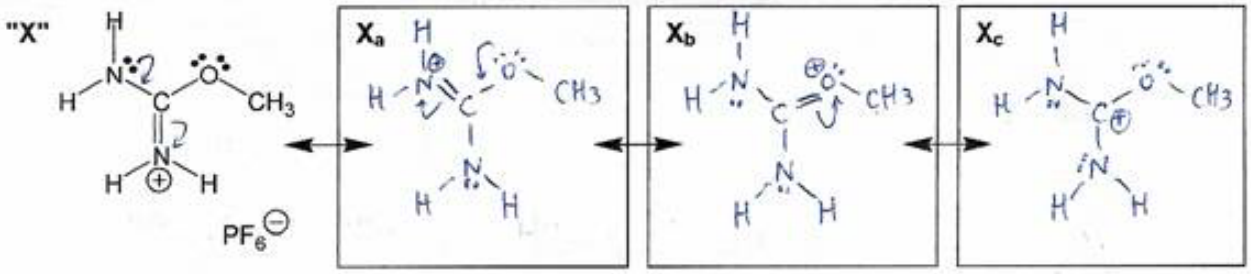


Isomer B can also form H-bonds, but the ether group can only accept H-bonds, so I expect overall this isomer would be less soluble than C.

CHEM 221 Fall 2003 Section 02 MIDTERM #1-A Name: answer key

 # 8. a) (3 Marks) There are three other significant resonance contributors for molecule **"X"** shown below. Draw them in the boxes provided. You do not need to draw the PF_6^- anion.

→ all atoms in same places; only πe^-s can move



b) (3 Marks) Rank the four structures **X**, $\mathbf{X_a}$, $\mathbf{X_b}$, and $\mathbf{X_c}$ according to how much they contribute to the real structure of the molecule. Give a reason why the most important contributor is so stable, and why the least important contributor is so unstable.

Most important ... **Least important**

X = X_a > X_b > X_c

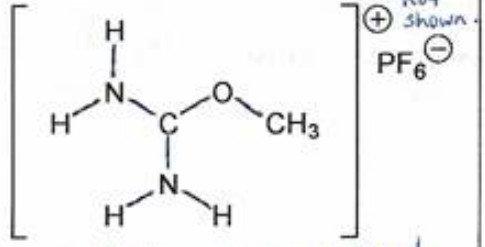
Same bonding arrangement ∴ identical in energy (stability)

Why so stable?
- all atoms have full valence
- positive formal charge is on N rather than O, which is more electronegative ∴ more likely to carry lone pair than N in this situation.

Why so unstable?
- Carbon has open shell i.e., only 6 valence e^-.

c) (2 Marks) Considering these resonance contributors, how do you think the molecule "really" looks? In the box on the left, the connectivity in molecule **"X"** is indicated by dotted lines. **Your task is to represent the 3-dimensional (3-D) representation of structure of "X" by writing over the dotted-lines: use lines, dashes and wedges to indicate spatial orientation with respect to the page.** Describe this 3-D structure by filling in the blanks in the other box (you can number the atoms in the structure for clarity).

How I think "X" looks in 3-D: Geometry only! π bonds not shown.



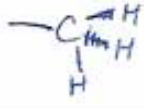
all planar except CH_3!

These bond will NOT rotate freely:
N-C, N-C, C-O (bond order > 1)

These atoms will be in the same plane:
H_2N, H_2N, C, O, C but NOT the CH_3's H atoms.

The reason for this is:
- delocalization of π-electrons over overlapping p-orbitals (extended π-system)
- if rotation occurred, overlap between p-orbitals would be broken! Requires high energy to occur.

Should have drawn:



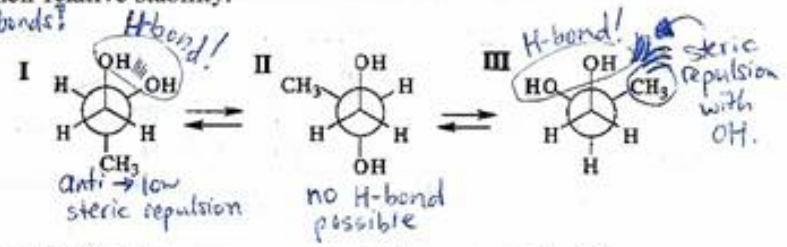
note there is free rotation about the O–C bond, so on average none of the C-H bonds are coplanar with O-C bond } i.e. the methyl group spins!

CHEM 221 Fall 2003 Section 02 MIDTERM #1-A Name: answer key

 # 9. (___/ 4 Marks) CIRCLE YOUR CHOICE. The three staggered forms of 1,2-propanediol are represented here as Newman projections. Taking into account **both** steric and electrostatic interactions between substituents, rank the conformers according to their relative stability.

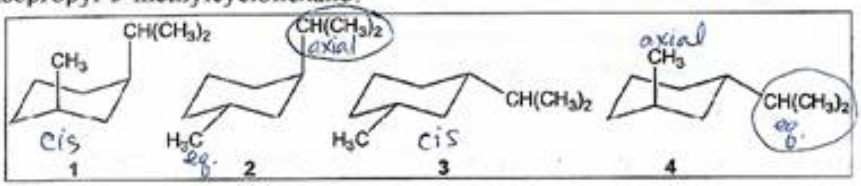
↳ here have INTRAmolecular H-bonds!

a) most stable **III < II < I** least stable
b) most stable **III < I < II** least stable
c) most stable **II < III < I** least stable
(d) most stable **I < III < II** least stable
e) most stable **I < II < III** least stable



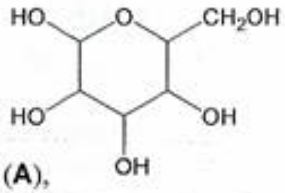
 # 10. (___/ 3 Marks) CIRCLE YOUR CHOICE. Which structure represents the most stable chair conformation of *trans*-1-isopropyl-3-methylcyclohexane?

a) 1 X cis
b) 2 trans
c) 3 X cis
(d) 4 trans



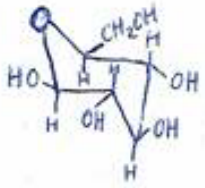
largest substituent in equatorial position.

 # 11. (___/ 5 Marks) The structure of glucose includes a six-membered ring. The relative orientations of the ring's substituents has not been shown in the drawing here, but the information in part (a) will allow you to figure it out.

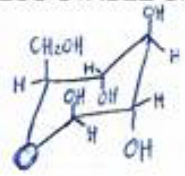


a) In the most stable conformation of glucose, the molecule adopts a chair conformation where all the substituents are equatorial. Draw this conformation (**A**), and show what the molecule would look like in the "flipped" chair conformation (**B**).

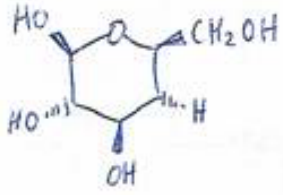
MORE STABLE CHAIR: **A** all equatorial



LESS STABLE CHAIR: **B** all axial



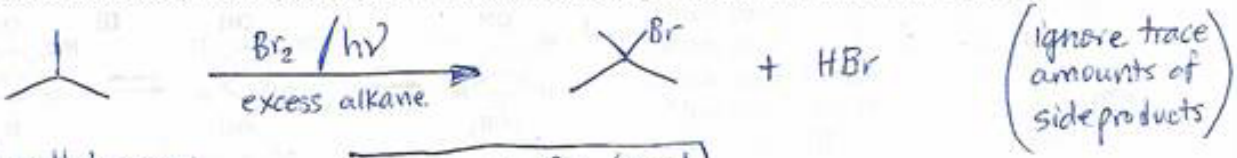
b) Draw a planar representation of glucose (like that shown at the top of the question) that shows the dashes and wedges needed to illustrate the relative orientation of the substituents.



CHEM 221 Fall 2003 Section 02 MIDTERM #1-A Name: answer key

 # 12. (___/ 8 Marks) You are asked to prepare 2-bromo-2-methylpropane, starting with an alkane precursor.

a) What reagents and reaction conditions (*e.g.*, hot/cold, light/dark, relative amounts of reagents; we'll learn about solvents later) would you choose? Write a reaction equation that describes your choices.



2-methylpropane

(or, could use Br_2 / heat with excess alkane)

b) Would a significant amount of undesired products also form? Explain, and identify any undesired products you are talking about and how they would form.

In 2-methylpropane contains 1 3° H and 9 1° H's. Bromine radicals are highly selective for 3° H atoms, so they will preferentially abstract the 3° H to form the desired product. However, because there are 9 1° H's, statistically speaking it is still probable that a small amount of 1-bromo-2-methylpropane will form. However, it is much more difficult to abstract a 1° H because of the inherent instability of 1° radicals, and Br•'s are not reactive enough to do it frequently.

extra info: beyond course scope...
product distribution for bromination: 1°: 9 × 1.0 = 9 ÷ 1609 = <1%
3°: 1 × 1600 = 1600 ÷ 1609 = >99%
1609 total

c) Would your answer to (b) be the same if you were talking about preparing 2-methyl-2-chloropropane instead? Explain.

Cl radicals are much more unstable (reactive) than Br radicals, because of their smaller size. Thus, they are less selective for highly substituted abstraction sites, and a product ratio closer to that predicted statistically occurs. For this reason, a much larger amount of 1-chloro-2-methylpropane would form. In fact, given the 9:1 ratio of 1°:3° H's in the molecule, the 1° chloride product would probably even be the major product. ← this could be predicted fairly accurately using the relative reactivity values for Br• vs Cl• towards 1°, 2°, 3° H's, but you are not responsible for memorizing those numbers! (see section 9.3 if interested)

---THE END---

For Cl•: 1°: 9 × 1.0 = 9.0 ÷ 14 total = 64% 1° chloride
3°: 1 × 5.0 = 5.0 ÷ 14 total = 36% 3° chloride
14 total