Dr. Steven Pedersen October 5, 2015

Chemistry 3A

Midterm 1

Student name: ANSWER KEY

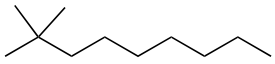
Student signature: _____

Problem 1	_____	(18 pts)
Problem 2	_____	(16 pts)
Problem 3	_____	(22 pts)
Problem 4	_____	(20 pts)
Problem 5	_____	(18 pts)
Problem 6	_____	(10 pts)
Problem 7	_____	(16 pts)
Problem 8	_____	(30 pts)
Total Points	_____	(150 pts)

No Calculators Allowed
No Molecular Models Allowed
Be Sure Your Exam has 10 Pages

1. There will be NO partial credit for this problem. Avoid careless errors by checking over your answers. (18 pts)

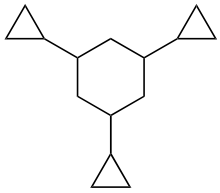
A. Provide a systematic (IUPAC) name for each of the following compounds. Use common nomenclature for any branched substituents.



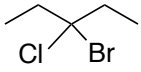
2,2-dimethylnonane

or

8,8-dimethylnonane



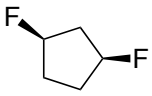
1,3,5-tricyclopropylcyclohexane



3-bromo-3-chloropentane

or

3-chloro-3-bromopentane



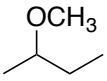
cis-1,3-difluorocyclopentane

or

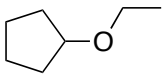
cis-1,4-difluorocyclopentane

B. The IUPAC nomenclature for ethers is quite straightforward. Two examples are provided below. Using your extrapolative skills, draw the structure of each compound in the boxes provided.

The examples:

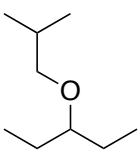


2-methoxybutane

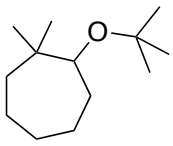


ethoxycyclopentane

Extrapolate:



3-isobutoxypentane

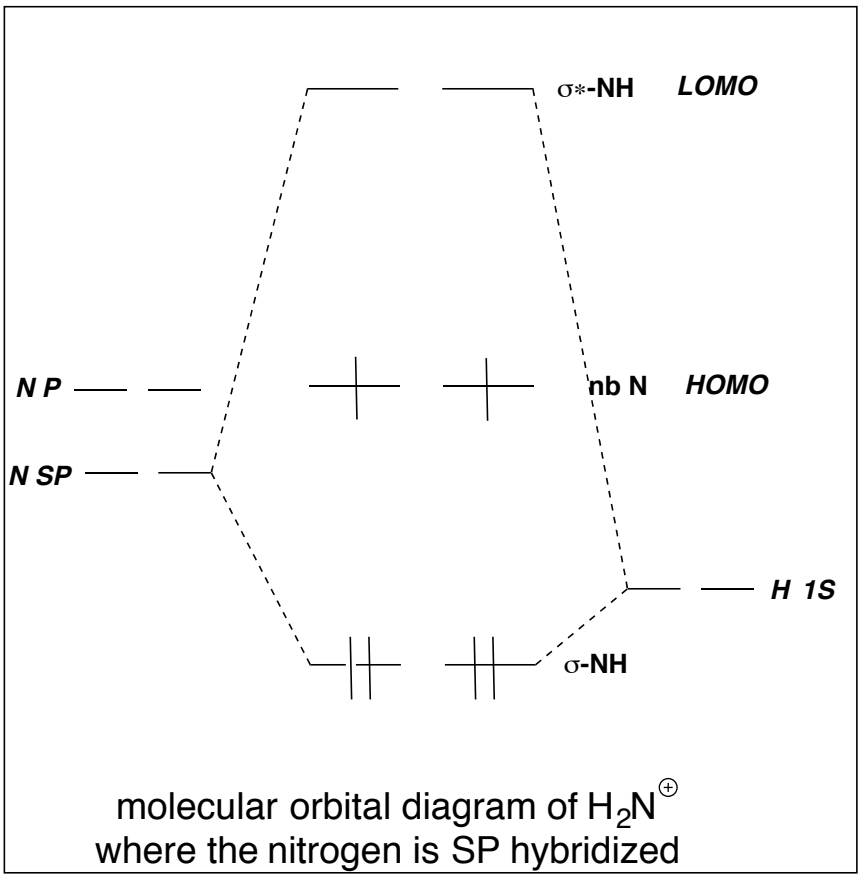


1,1-dimethyl-2-*tert*-butoxycycloheptane

2. (16 pts)

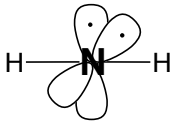
A. Construct a molecular orbital diagram for H_2N^+ using the following guidelines and labeling schemes. BE SURE TO INCLUDE EVERYTHING ASKED FOR BELOW.

- ASSUME that the nitrogen is SP hybridized.
- Indicate the relative energy levels of any atomic and hybrid orbitals on both sides of the diagram.
- Clearly indicate which orbitals are being combined to make molecular bonding orbitals.
- Label all the levels as σ, π, nb (non-bonding) etc.
- Fill in all of the electrons.
- Label the HOMO and LUMO



molecular orbital diagram of $H_2N^{\oplus}$
where the nitrogen is SP hybridized

B. Draw a picture that best represents what the structure of H_2N^+ looks like based on the MO diagram you drew. For the N-H bonds, you do not need to show orbitals. Clearly draw any non-bonding orbitals and make sure all angles between bonds and orbitals are clearly illustrated.

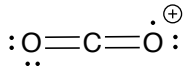


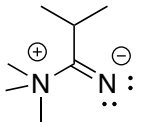
3. (22 points)

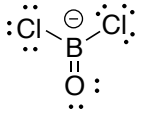
A. Provide the ideal hybridization for each molecule below. ASSUME that all valence electrons not involved with bonding are paired (note, if there are valence electrons not involved in bonding, they are not shown).

	$BH_2^{\oplus}$	$BH_2^{\ominus}$	CH_2	$NH_4^{\oplus}$	$2\ BeH_2^{\ominus}$
ideal hybridization	*SP*	*SP²*	*SP²*	*SP³*	*SP²*

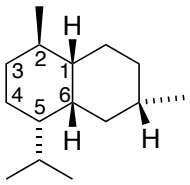
B. Add correct formal charges where necessary (be sure they are placed on the correct atom). ASSUME that ALL electrons not involved in bonds are shown. Wrong charges cancel correct charges on each molecule.





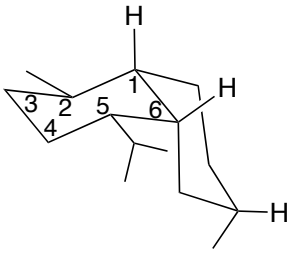


C. Amorphane is a "generic" bicyclic compound found in many plants. Below is the structure of one type of amorphane. Redraw this in its chair-chair conformation (that is, both chairs need to be clearly shown). One of the chairs is already provided. Any hydrogen atoms that are shown in the left hand structure MUST be shown on the chair-chair structure. Be sure to use the numbering system shown!



amorphane

Complete your drawing beginning with this chair conformer. The second chair must be clearly illustrated.

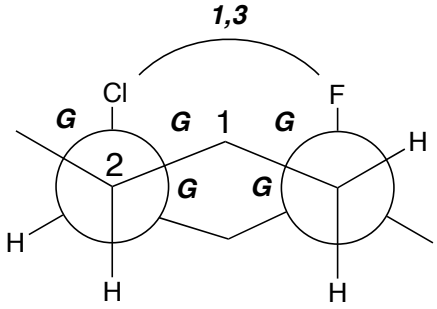


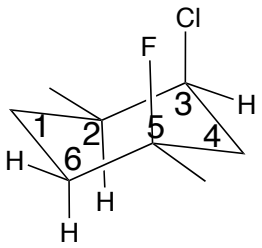
D. What is the molecular formula for the amorphane shown in Part C (above)? Provide your answer in the box below.

$C_{15}H_{28}$

4. (20 points)

A. Below is a double-barreled Newman projection. On the chair provided, draw the structure this projection represents making sure to use the numbering system provided. Any hydrogen atoms shown in the Newman projection must be shown on the chair structure.



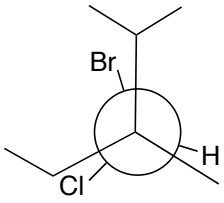


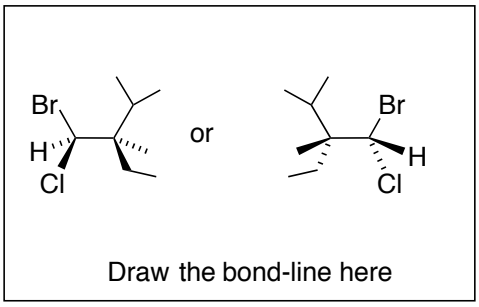
"Double-barreled" Newman projection.

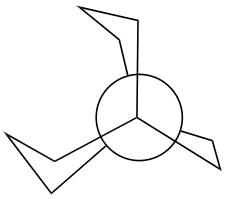
B. On the Newman structure in Part A, indicate all gauche interactions by writing the letter G in between the substituents involved. Wrong answers cancel right answers.

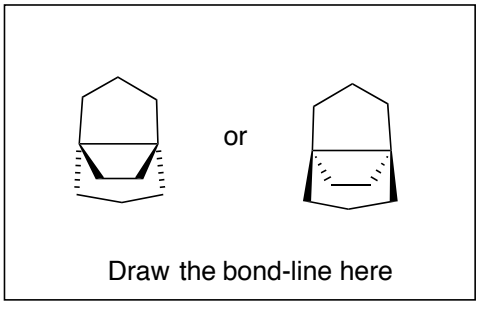
C. On the Newman structure in Part A, indicate all 1,3-diaxial interactions (do not include any that involve hydrogen atoms) by drawing a curved line between the two substituents and writing "1,3" above or below the curved line. Wrong answers cancel right answers.

D. Draw a bond-line structure that corresponds to the conformation depicted in the Newman projections shown below.







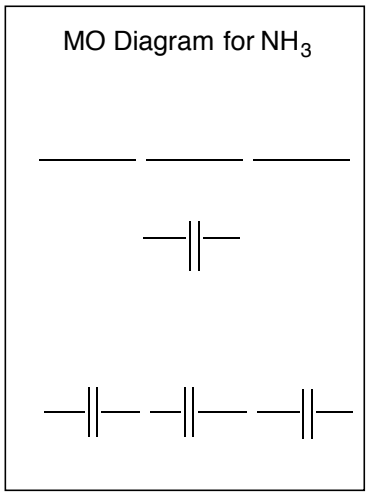


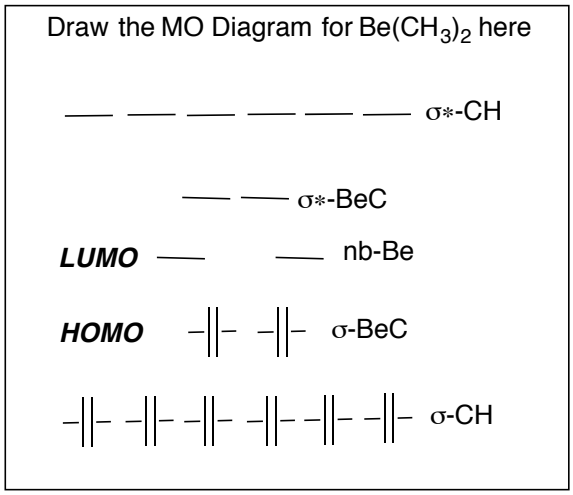
5. (18 points)

A. The MO diagram for ammonia (NH_3) is provided below. In the box next to it draw (do not construct) the MO diagram for $Be(CH_3)_2$. Note that C-H bonds are stronger than C-Be bonds.

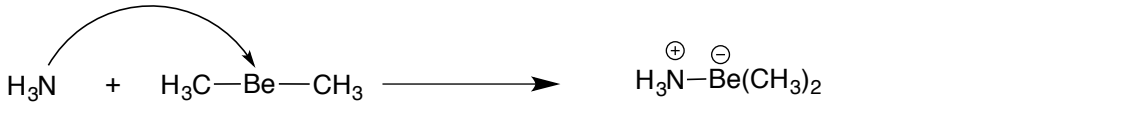
In the second box, be sure to include the following:

- Label all the levels in this new diagram as σ, π, non-bonding (nb), σ^*, etc., making sure to include the atoms involved in bonds or associated with non-bonding orbitals (e.g. σ-CH, nb C).
- Fill in the electrons on the new diagram.
- Label the HOMO and LUMO.





B. A reaction between ammonia and $Be(CH_3)_2$ is shown below. Based on your completed MO diagrams above and Frontier Molecular Orbital (FMO) theory, predict the product(s) you would expect to get from this reaction. Use a curved arrow(s) to signify electron movement (i.e. arrow-pushing of electrons). To receive any credit for this Part, your product(s) must be consistent with what FMO would predict based on the diagrams you completed in Part A.

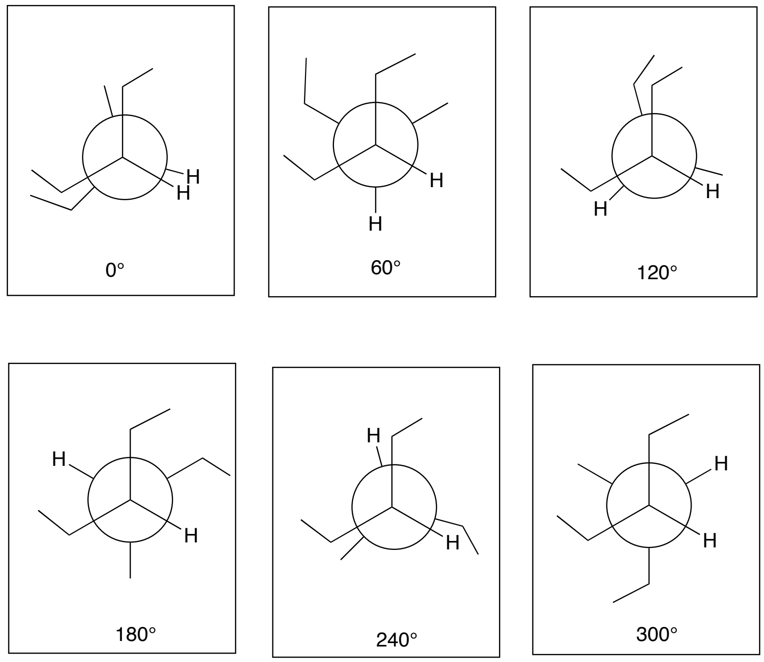


Use arrow-pushing here to show how you arrived at the product(s) here

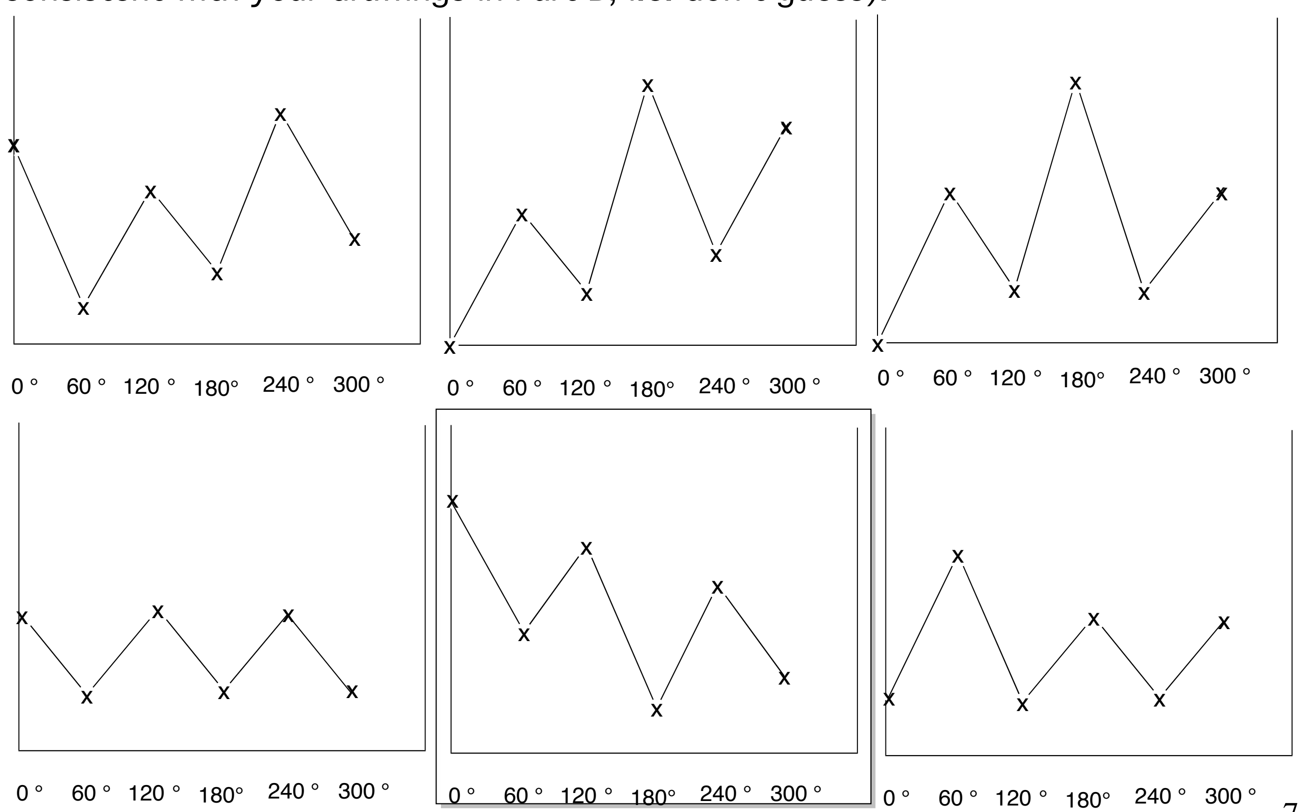
6. (10 points)

A. Starting with the Newman projection shown below, draw the five remaining Newman projections representing 60° rotations about a carbon-carbon single bond. You must follow the instructions below:

- Hold the front carbon constant
- Rotate the back carbon clockwise



B. Which potential energy diagram matches the Newman projections you drew in Part A? Circle one. (you will receive no credit for this part if your answer is not consistent with your drawings in Part B, i.e. don't guess).



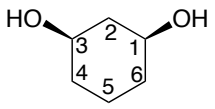
7. (16 points)

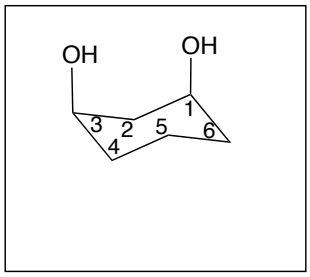
A. In the box labeled "chair structure" translate the flat-ring structure directly above it to a chair, using the numbering provided. In the box labeled "ring-flipped chair structure" draw the ring-flipped conformer of the structure shown in the box labeled "chair structure."

B. Using the values from the Table on your handout calculate ΔG for this equilibrium. Clearly show your work in the appropriately labeled box. Place your final numerical value in the box labeled ΔG =.

You will receive no credit for your answer if you do not show your work!

C. Based on your answer for ΔG, use arrows to indicate which side the equilibrium would favor.

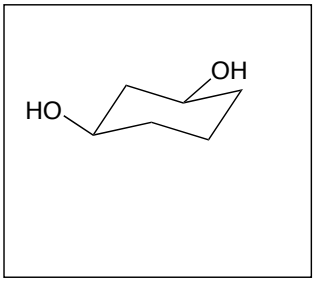




chair structure

ΔG = -1.88

express the direction of K here



ring-flipped chair structure

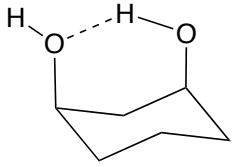
Show your work for calculating ΔG here

2 (OHax to OHeq) = 2 x -0.94

= -1.88

D. In reality, K = 0.9, for this particular equilibrium. The explanation involves hydrogen-bonding, like that found in water. Using a picture and a few words, explain how hydrogen-bonding can account for this this unexpected result. Keep your answer within the space below (do not write on the back of this page).

As can be seen from the structure below, hydrogen-bonding is possible between the two axial hydroxyl groups (i.e. the OH groups). This must stabilize the axial groups relative to the more favorable equatorial groups where such intramolecular hydrogen-bonding is not possible.

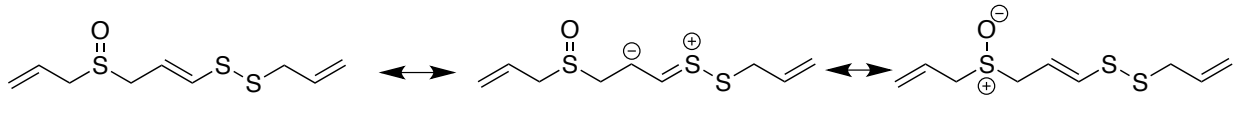


Cooking Time!

8. (30 points)

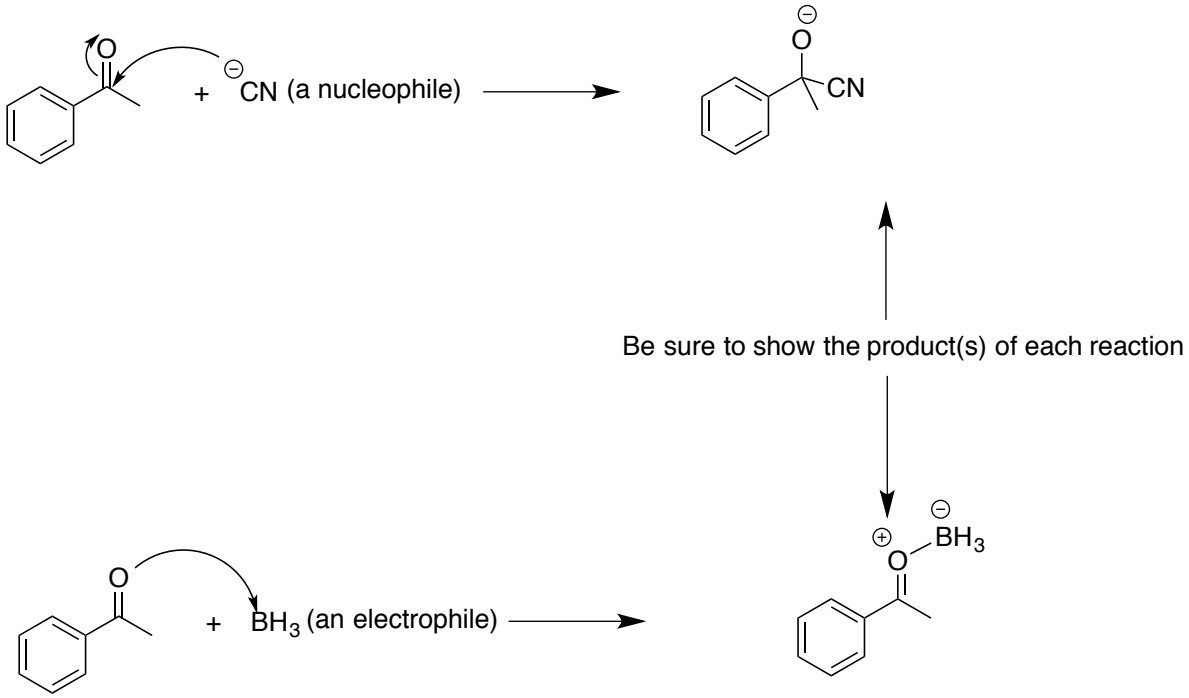
Fall is upon us and cooking (and eating) takes center stage in many households. The following questions all involve compounds found in common cooking ingredients.

A. Draw TWO additional REASONABLE and VALID resonance structures for the compound shown below. Do not draw more than two resonance structures.



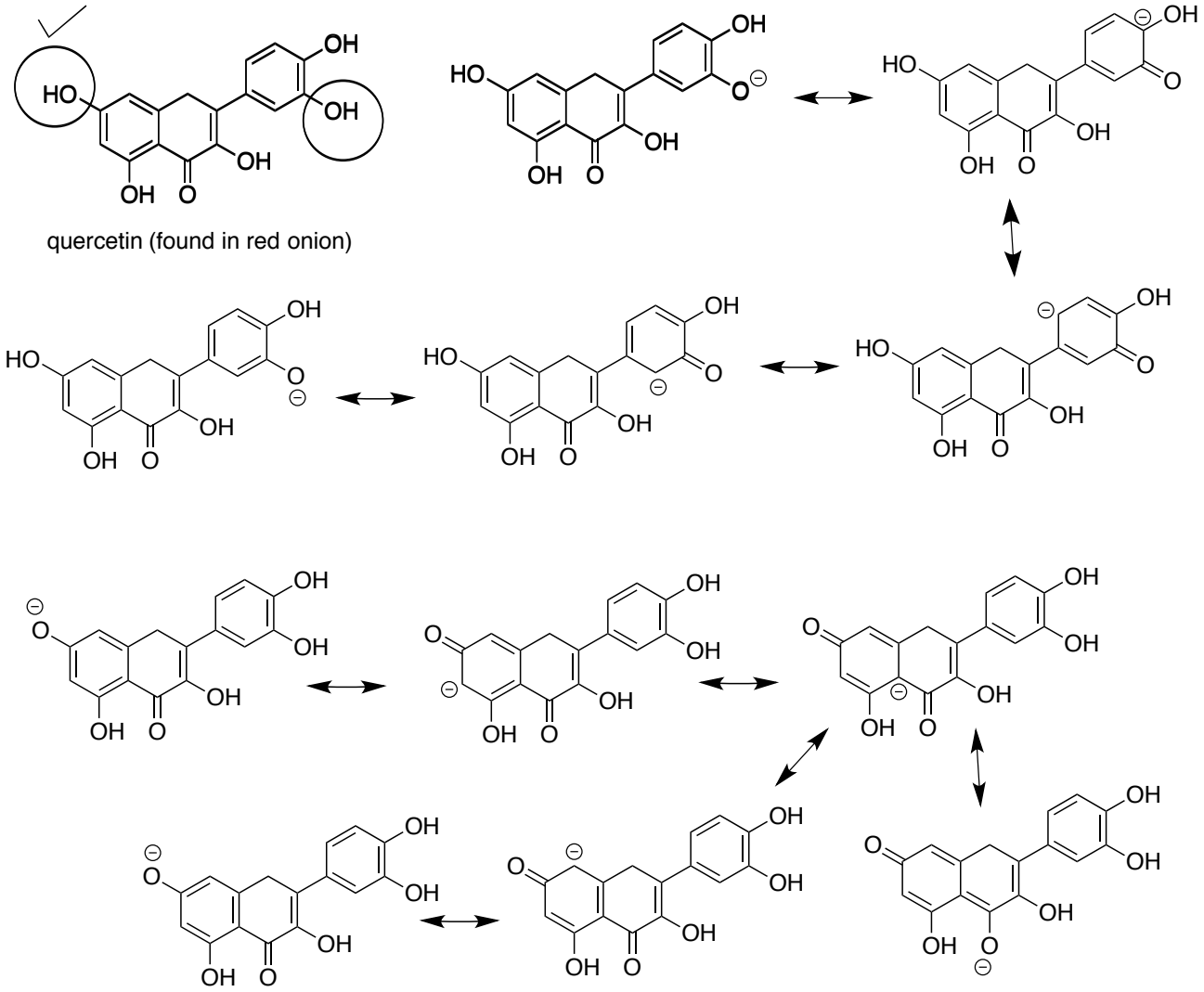
ajoene (formed in freshly ground garlic)

B. Acetophenone is found in black pepper. Using arrow-pushing, indicate where acetophenone will react with each of the reactants shown AND show the product(s). You can use resonance structures to help guide you to your conclusion. If you do so, you must use arrow-pushing to indicate how you went from one resonance structure to the next.



Continued on next page

C. Which one of the two circled OH groups has the lowest pKa (place a check mark next to your choice)? You will only receive credit by providing an explanation using words and drawings to illustrate your choice (relative to the other possibility). Keep you explanation and drawings within the space provided. Do not continue your answer on the back of this page.



quercetin (found in red onion)

When one examines the resonance structures for each conjugate base, the one with the most resonance structures will be the most stable and hence its acid will be the most acidic (i.e. lowest pKa). As can be seen the conjugate base of the hydroxyl group that is checked has one additional resonance structure AND in that structure, the lone pair is on another oxygen atom, which is preferred over being on a carbon due to electronegativity.