Chemistry 3A – Exam #1

Student Name: Pete's Key

Student ID Number: _____

Point Breakdown

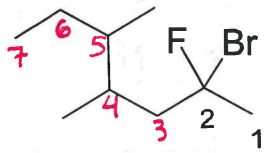
Problem 1	_____	/ 18
Problem 2	_____	/ 16
Problem 3	_____	/ 18
Problem 4	_____	/ 13
	_____	/ 18
Problem 5	_____	/ 18
Problem 6	_____	/ 21
	_____	/ 17
	_____	/ 11
Total	_____	/ 150

Check that you have 9 pages with questions on them.

You will have 120 minutes for this exam.

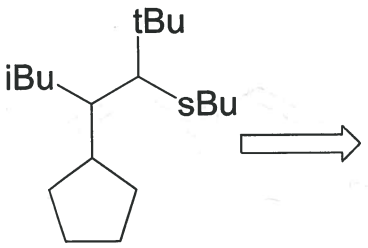
REMEMBER: Opposites attract, formal charges are required, and the octet rule is super important

1. A. Provide a systematic name for the following molecule. Use common names where appropriate. Continue numbering the carbons based on the first 2 carbons. (2 pts)

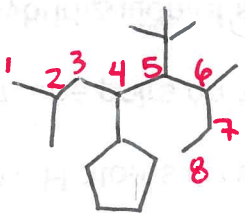


2-bromo-2-fluoro-4,5-dimethyl heptane

1. B. Specifically show the full bond-line structure of the molecule below. For example, instead of "Me", use an end of a line. (2 points)



shorthand

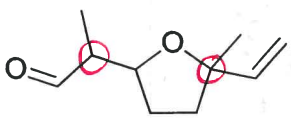


bond-line

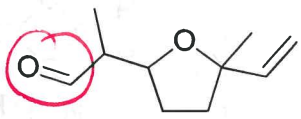
1. C. Provide a systematic name for the molecule you drew in 1.B. above. Part of the name has been provided for you. Make sure your number scheme matches the name provided. (2 points)

2,6-dimethyl- 4-cyclopentyl-5-tertbutyl octane

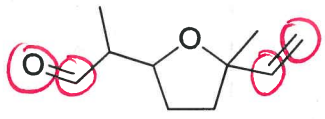
1. D. Lilac Aldehyde has many functional groups. On the molecule in each box,circle the functional groups or types of atoms named. If it is not present, write NONE. (12 points)



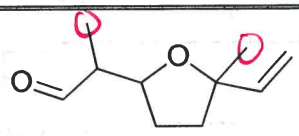
two tertiary carbons



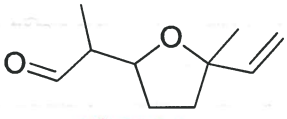
aldehyde



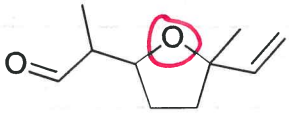
all sp^2 hybridized atoms



all primary carbons



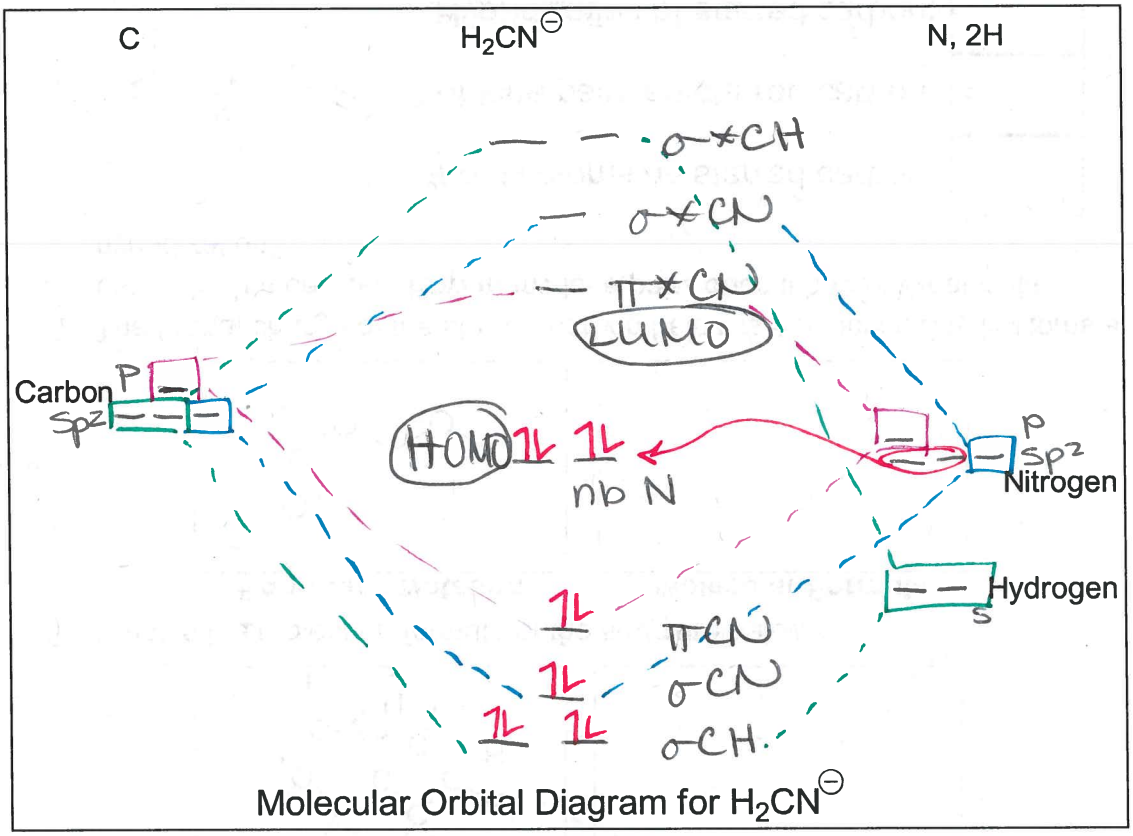
NONE
alcohol oxygen



ether oxygen

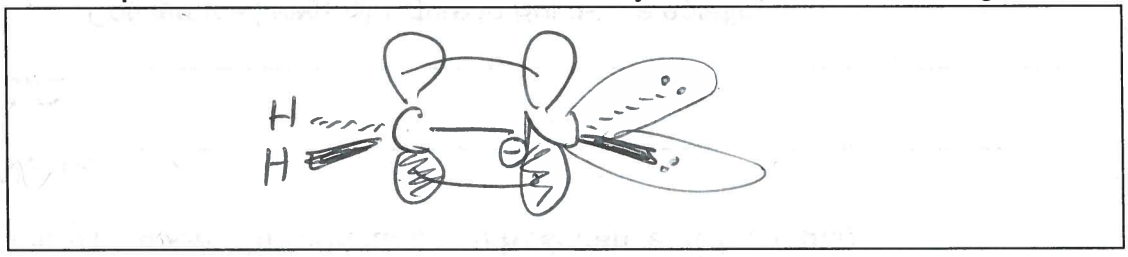
2. Construct the molecular orbital diagram for the molecule $H_2CN^{\ominus}$, using the following guidelines and labeling schemes. The carbon is the central atom. (16 pts)
   a. Assume the nitrogen and carbon atoms are both **sp^2** hybrized.
   b. Indicate the relative energy levels of any atomic and hybrid orbitals on both sides of the diagram and label them (s, sp^2, etc.).
   c. Clearly indicate which orbitals are being combined to make MOs
   d. Label all of the MO levels (σCH, πOO, π^*FCl, n.b. N, etc.)
   e. Fill the MOs with the correct number of electrons
   f. Label the HOMO and LUMO

2H, N C ⊖
2 5 4 1 = 12e⁻

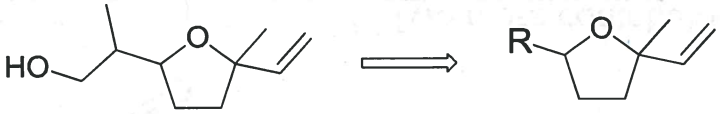


Molecular Orbital Diagram for $H_2CN^{\ominus}$

   g. Draw the 3D representation of $H_2CN^{\ominus}$ below. Feel free to use our template from class. You must clearly show all formal charges.

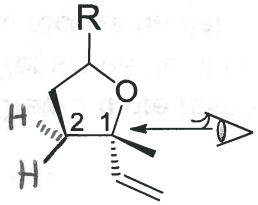


3. Lilac Alcohol is responsible for the distinctive scent of lilacs.

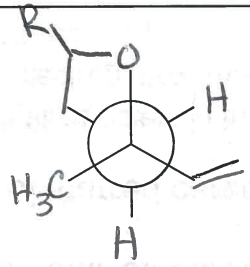


Lilac Alcohol Lilac Alcohol

3. A. Add the hydrogen atoms, with proper tetrahedral shape, to carbon 2 of Lilac Alcohol below. (2 points)



Add hydrogens to carbon 2



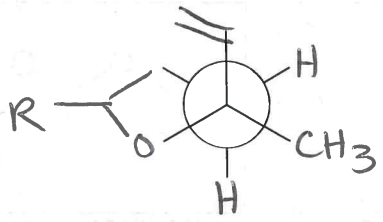
0°

Newman from C1 to C2

3. B. Draw a Newman Projection along the C1-C2 bond as indicated by the eye. Use the projection template provided above. (3 points)

3. C. Rotate the front carbon 120 degrees counter clockwise using the template provided below. (3 points)

Front Carbon 120° CCW



Newman from C1 to C2

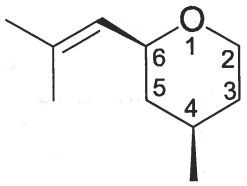
3. D. Describe the steric interactions at 0° and 120°. Use the abbreviations "Me" for the methyl group, "Alk" for the alkene, "O" for the oxygen, and "ring" for the oxa-cyclopentane ring. Use "E" and/or "G" for eclipsing and/or gauche interactions. (6 points)

Rotation Angle	Steric Interactions
Front Carbon 0°	G: O, ring ; G: ring, Me
Front Carbon 120° CCW	G: Alk, ring ; G: ring, O

3. E. Is it possible to rotate the front carbon 120° CW? Explain. (4 pts)

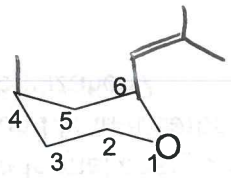
Yes / (No) because: Ring strain	(3 word limit)

4. (-) *cis*-Rose-oxide is the molecule responsible for the charateristic scent of roses. It is a very minor, but potent, component of roses.



(-) *cis*-Rose-oxide

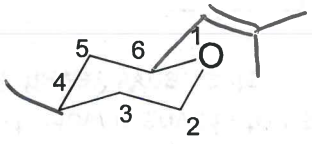
4. A. Draw the substituents of (-) *cis*-Rose-oxide in the proper orientation on the chair structure provided below. (3 points)
4. B. Draw the chair-flipped structure in the box to the right. (3 points)
4. C. Using the data provided at the bottom of the page, calculate the ΔG of the chair-flip. Please take substituent-substituent interactions into account. Place that value in the appropriate box. Show your work to receive any credit. (5 points)
4. D. Based on your ΔG, add an appropriate equilibrium arrow. (2 points)



Chair

ΔG = -6.0

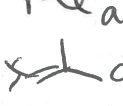
equilibrium arrow

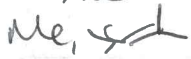


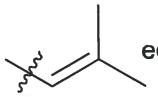
Chair-flipped structure

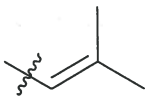
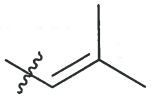
Show work:

$Me_{ax \rightarrow eq} = -1.70$

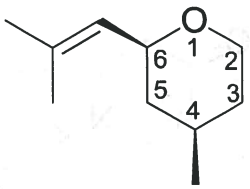
 $_{ax \rightarrow eq} = -1.80$

1,3 diaxial Me,  $= -2.5$

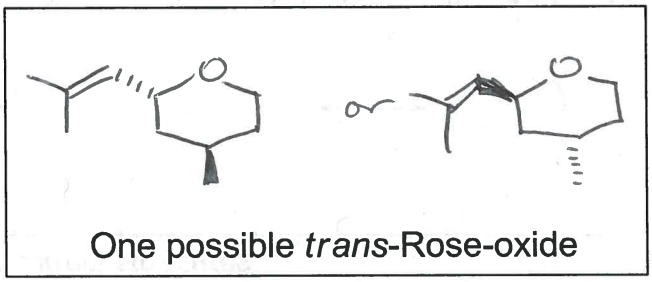
Substituent	ΔG° (kcal/mol)	Substituent	ΔG° (kcal/mol)
$Me_{eq \rightarrow ax}$	1.70	 eq→ax	1.80

Substituent-substituent interaction	Gauche: Me, 	1,3-diaxial: Me, 
Energy Cost	3.0 kcal/mol	2.5 kcal/mol

4. E. There are two possible *trans*-Rose-oxide structures. Draw one of them in the box below. (3 points)

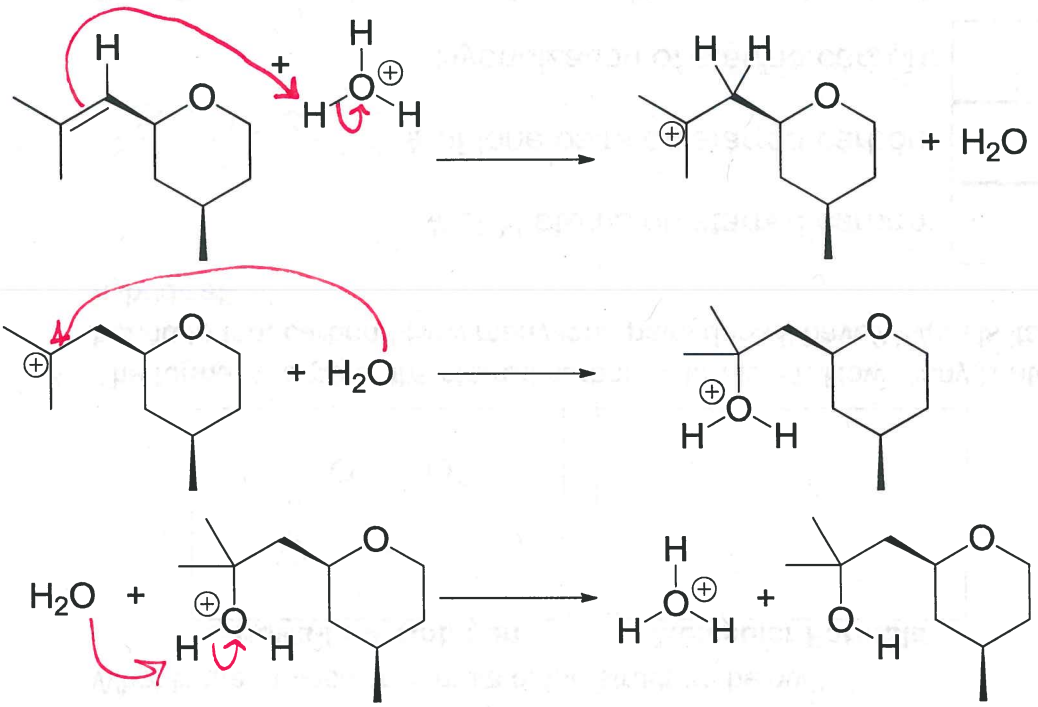


(-) *cis*-Rose-oxide



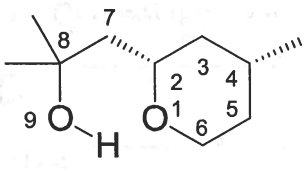
One possible *trans*-Rose-oxide

4. F. Draw the necessary electron-pushing arrows . (10 points)

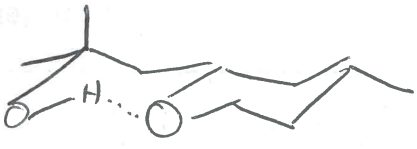


4. G. Draw the compound below in an all chair conformation with an intramolecular hydrogen bond AS A DOTTED LINE between the alcohol proton (10) and the oxygen of the ring (1). (5 points)

Flat-Ring

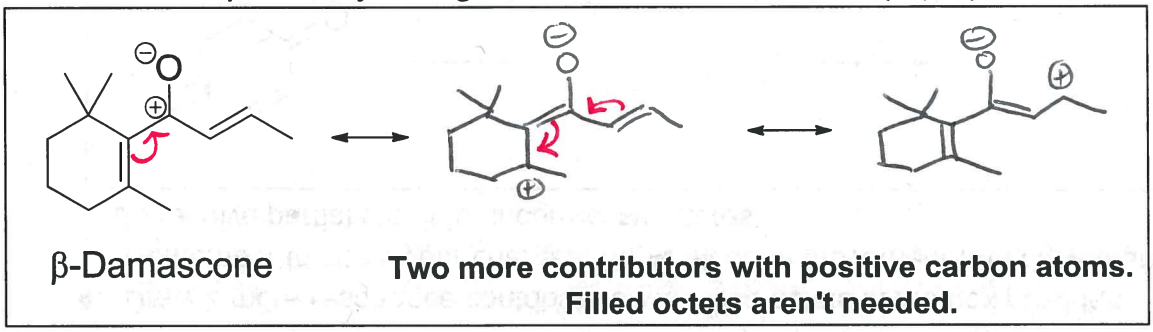


Chairs clearly showing intramolecular H-Bond between (10) and (1).



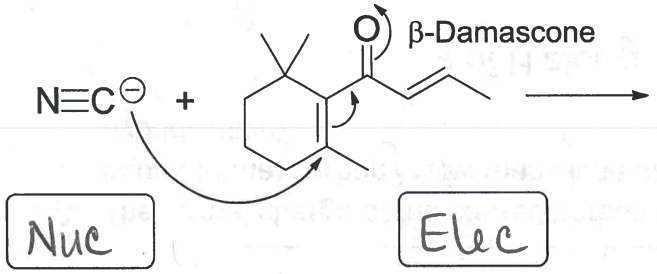
hint: it looks like trans-decalin

5. A. Draw two more resonance contributors of β-Damascone, a scent molecule in roses. Filled octets aren't necessary. Each contributor needs a positively charged carbon. Show arrows. (6 pts)

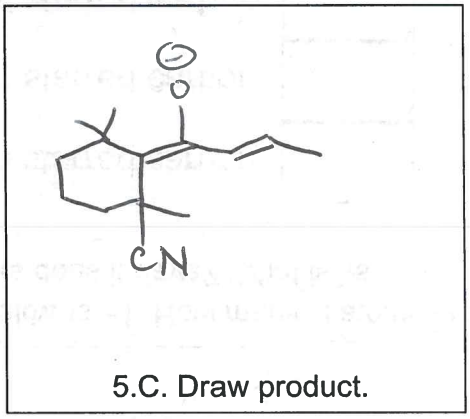


β-Damascone **Two more contributors with positive carbon atoms. Filled octets aren't needed.**

5. B. Label the nucleophile, "Nuc", and electrophile, "Elec", in the reaction below. (2 points)



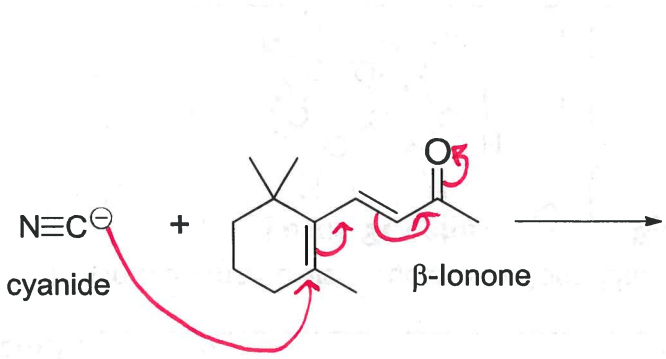
Nuc or Elec Nuc or Elec

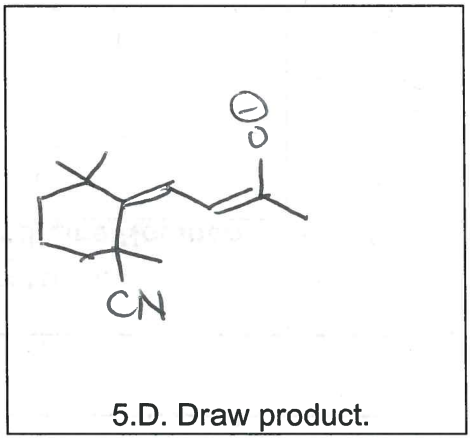


5.C. Draw product.

5. C. Show the product of the reaction above. (3 points)

5. D. Draw the product of the following two reactants creating a new bond between the partial positive carbon in the ionone ring and cyanide. Show the negative charge on oxygen in the product. (3 points)

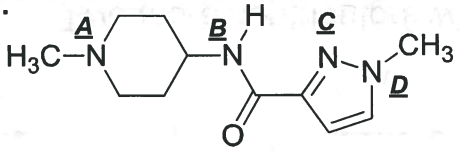




5.D. Draw product.

5. E. Add electron-pushing arrows to the reaction described in 5.D. (4 pts)

6. Granisetron is an antiemetic drug given to patients following chemotherapy to treat vomiting and nausea.



Granisetron

6. A. Define Bronsted Base in 8 words or fewer. Don't worry about complete sentences. (4 points)

Accepts a proton.

6. B. Indicate whether the INDUCTIVE EFFECT increases, decreases, or does not affect the basicity of each nitrogen atom in Granisetron. (8 points)

Nitrogen Atom	Effect of INDUCTIVE EFFECT on basicity
A	does not affect
B	decrease
C	decrease
D	decrease.

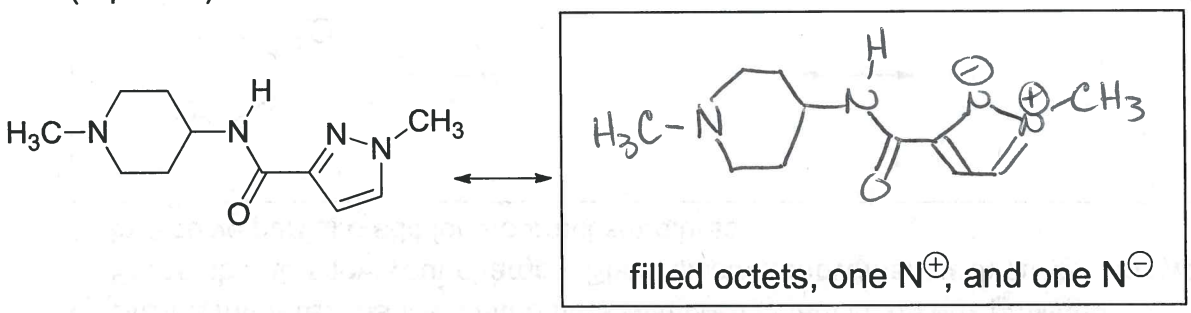
6. C. Based on the INDUCTIVE EFFECT, which nitrogen is most basic of Granisetron? Explain in 25 words or fewer. (5 points)

N_A is most basic b/c N_{B-D} are near EN atoms which pull e^- density away from them. N_A maintains its $\delta\ominus$.

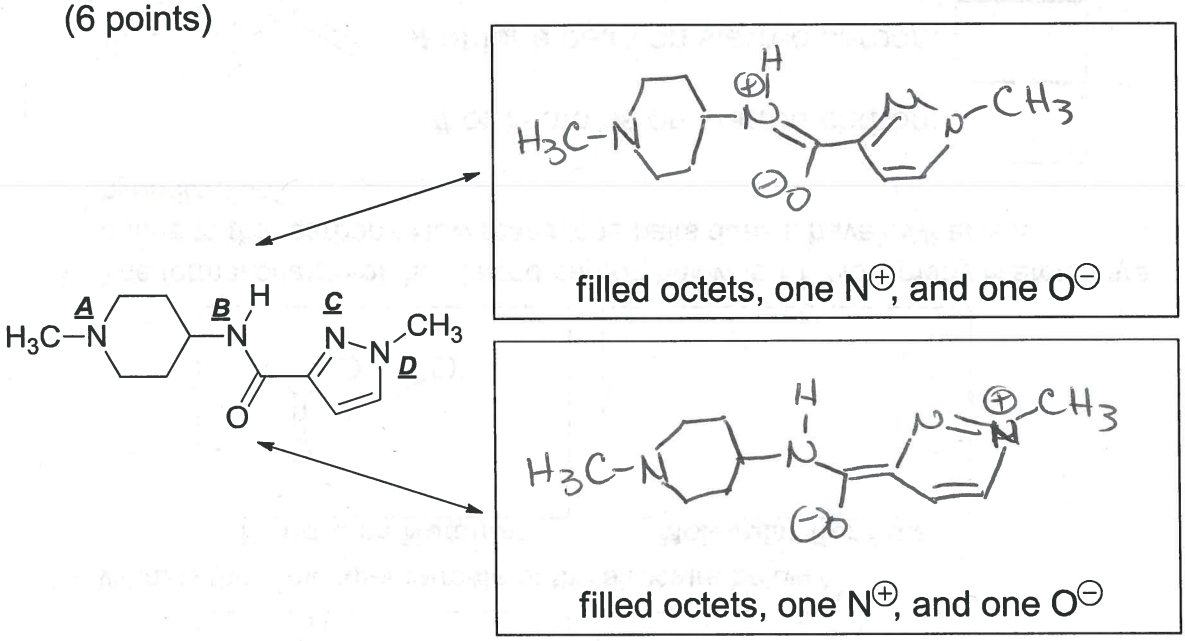
6. D. Define Nucleophile in 8 words or fewer. Complete sentences are not necessary. (4 points)

compound w/ an atom that is δ^-

6. E. Draw a resonance contributor of Granisetron with filled octets, one negatively charged nitrogen atom, and one positively charged nitrogen. (3 points)



6. F. Draw two resonance contributors of Granisetron with filled octets, one negatively charged oxygen atom, and one positively charged nitrogen. (6 points)



6. G. Indicate whether RESONANCE increases, decreases, or does not affect the nucleophilicity of each nitrogen atom in Granisetron. (8 pts)

Nitrogen Atom	Effect of RESONANCE on nucleophilicity
A	No effect
B	decreases
C	increases
D	decreases

6. H. Which two nitrogen atoms of Granisetron are <u>least</u> nucleophilic based on resonance? Explain in 25 words or fewer. (5 points)

B+D are least nucleophilic b/c resonance puts ⊕ on them, which would repel the electrophile.

6. I. Show the products of the electron-pushing arrows. (6 points)