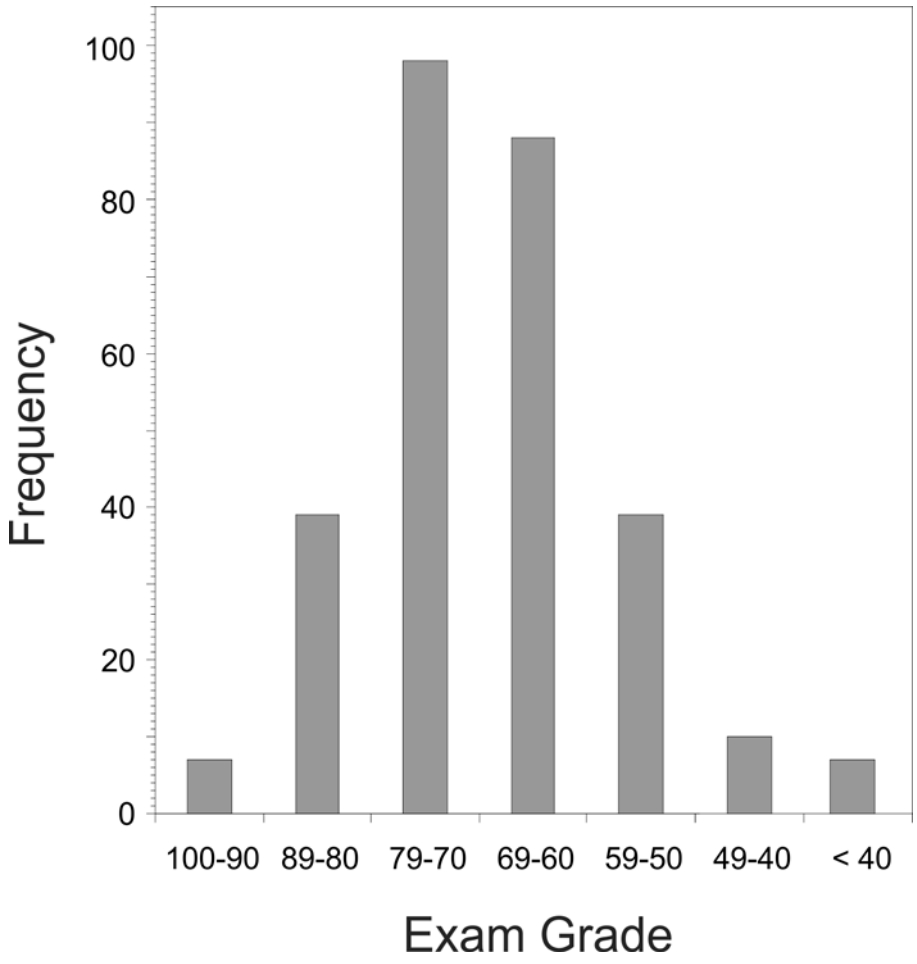
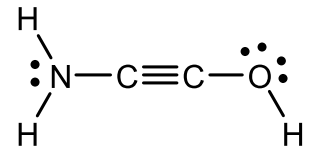
Exam 1
Answer Key

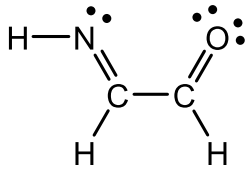
Exam 1 Mean:	72
Exam 1 Median:	74
Exam 1 St. Dev.:	14

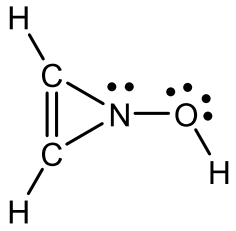


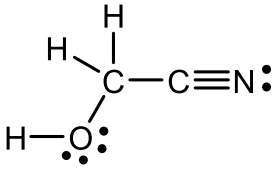
1. (6 pts) **Draw Lewis dash-bond structures** for two constitutional isomers that have molecular formula $\mathbf{C_2H_3NO}$, and that have **no formal charges** on any atom. Draw all atoms and lone pairs of electrons.

   Lots of possible answers to this question:









   ….and so many more.

   Rubric:

   3 points each correct structure (x 2, total of 6).

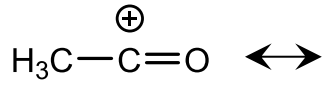
   -1 point for each missing electron pair, dot, bond, or atom.

   Structures that have formal charges, or that should have formal charges, receive no credit.

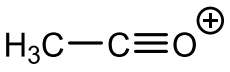
   1 point partial for drawing a structure with incorrect molecular formula—any molecular formula—but otherwise completely correct (and with no formal charges).

   If you drew same structure twice (e.g., as resonance structures), or you drew stereoisomers instead of consititutional isomers, we gave you credit for one but not the other.

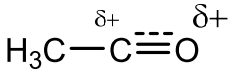
2. (18 pts) For each of the molecules on the left, draw as many of the best Lewis dash-bond resonance structures as there are boxes to put them in. (Feel free to omit lone pairs and C-H's, or draw them—your choice.) Then, below each resonance structure, describe whether each would be a major or minor contributor. Finally, draw a resonance hybrid that illustrates partial charges and multiple bonds.



resonance structure (3)



resonance hybrid (2)

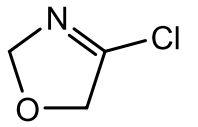


contribution: **minor** (1)

(major/minor?)

contribution: **major** (1)

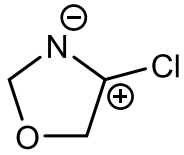
(major/minor?)



contribution: **major**

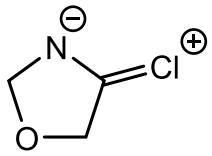
(major/minor?)

resonance structure (3)



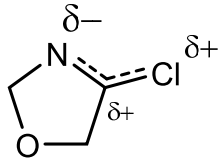
contribution: **minor**

resonance structure (3)



contribution: **minor**

resonance hybrid (2)



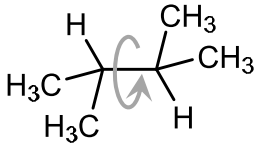
Rubric:

3 points for each resonance structure.
- *2 points for all charges correct and internally consistent.*
- *1 point for all correct bond orders.*

2 points for each consensus structure.
- *1 point for all partial charges correct.*
- *1 point for all correct bond orders.*

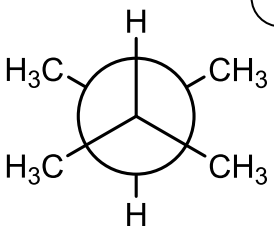
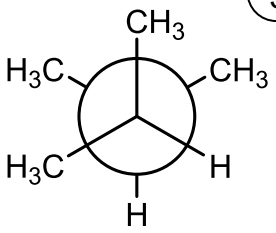
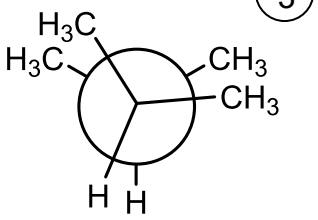
1 point for each contribution.
- *Just "major" and "minor" are enough. (No partial credit. Must have correct resonance structure for point.)*

3. (14 pts) 2,3-Dimethylbutane (molecule **1**, shown at right) is free to rotate about its central C-C bond.



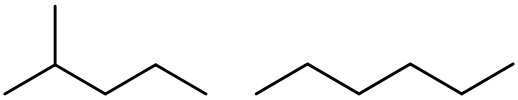
1

a. In the boxes below, draw Newman projections that illustrate the most stable, second-most stable, and least stable conformations of **1** with respect to rotation about the central C-C bond.

Newman projection for ***most stable*** *conformation*	*Newman projection for* ***second-most stable*** *conformation*	*Newman projection for* ***least stable*** *conformation*
3 	3  *(or its mirror image)*	3 

Rubric:
3 points for each correct Newman projection.
1 point partial for drawing <u>any</u> staggered projection for more stable, any eclipsed projection for less stable.

b. Molecules **2** and **3** are isomers of **1**; like **1**, they have chemical formula C_6H_{14}.



2 **3**

Are molecules **1**, **2**, and **3** **CONFIGURATIONAL ISOMERS** 2

or **STEREOISOMERS** ? *(Circle one.)*

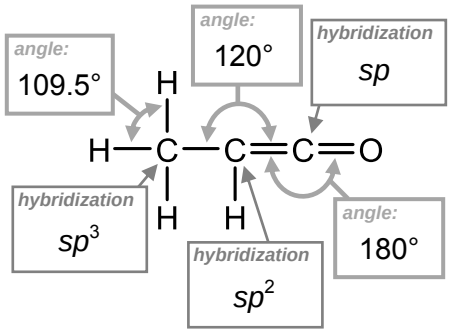
c. Each of the isomers **1-3** has its own heat of combustion (ΔH_c^0), which is the amount of energy given off when the molecule is burned to CO_2 and H_2O. Combustion is always exothermic, so ΔH_c^0 is always negative. In the boxes below, rank the molecules (**1-3**) in terms of their heats of combustion, from most exothermic to least exothermic.

most exothermic (most negative ΔH_c^0)				least exothermic (least negative ΔH_c^0)
	1	**2**	**3**	

3 for this sequence only.
No partial credit.

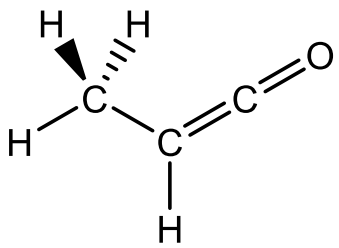
4. (18 pts) For each of the Lewis structures drawn below, in the boxes provided:
   - Draw Lewis wedge/dashed-bond structures that illustrate the most stable three-dimensional structure of the molecule. Draw all atoms, but feel free to omit lone pairs.
   - In the boxes provided, write the hybridization state for any atom heavier than hydrogen.
   - In the boxes provided, give any bond angle indicated by curved arrows in the original Lewis structure.

6

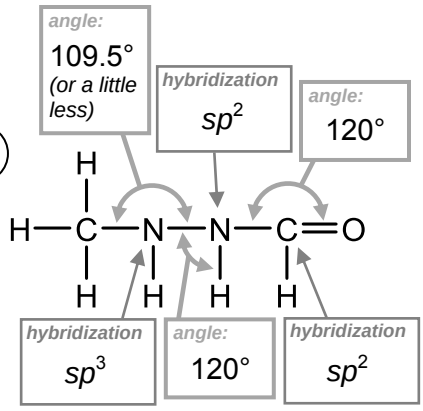


wedge/dashed-bond (3D) structure

3

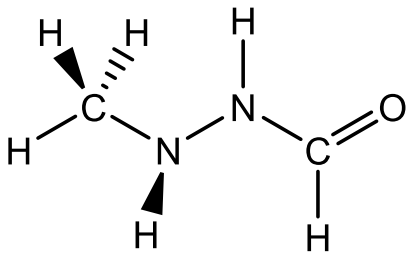


6



wedge/dashed-bond (3D) structure

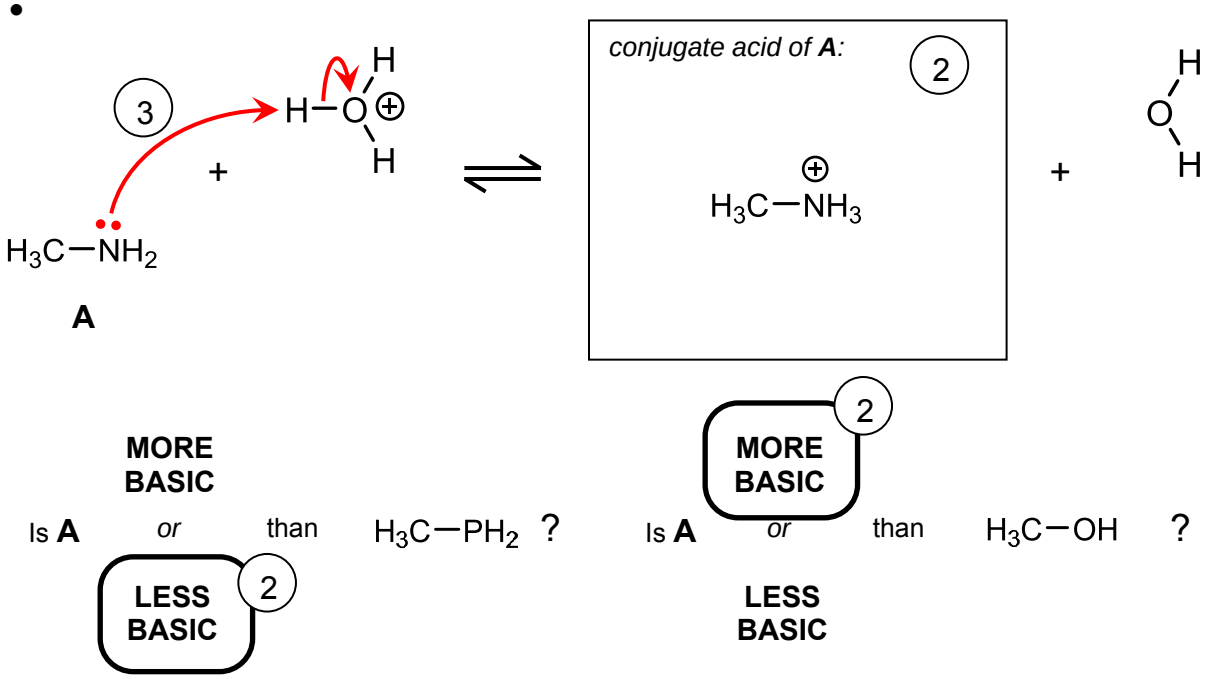
3



(or this could be hashed instead)

Rubric:
1 point for each bond angle and hybridization (12 total).
3 points for each 3-D structure (6 total).
-1 for each incorrect center or bond rotation (up to 3).

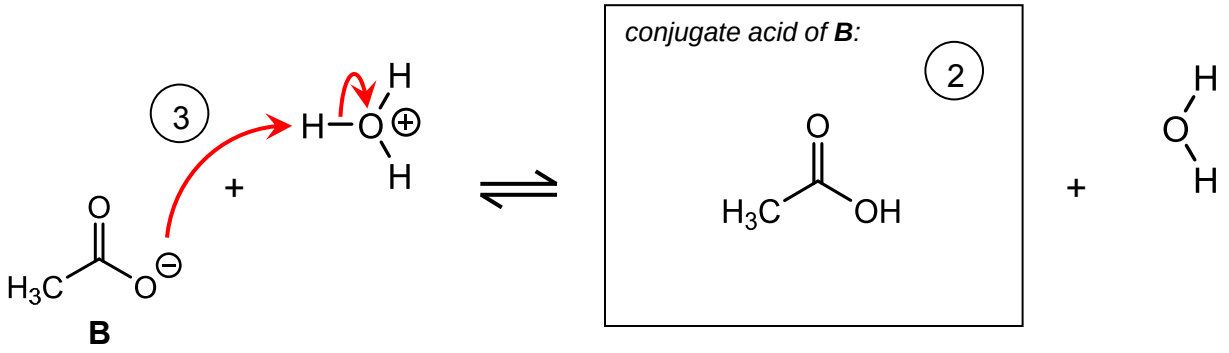
5. (18 pts) Molecules **A** and **B** below are both bases.
   - Using "electron pushing" (with double-barbed arrows), show how each base would be protonated in an acid-base reaction.
   - In the box on the right, draw the conjugate acid formed from each base.
   - Below each reaction, compare the basicity of **A**/**B** with other bases by circling the appropriate answer.
   -

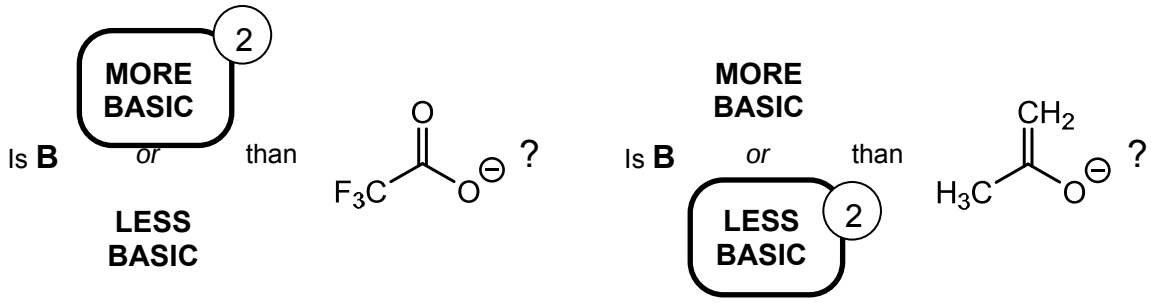


MORE BASIC
Is **A** *or* than H_3C-PH_2 ?
LESS BASIC
2

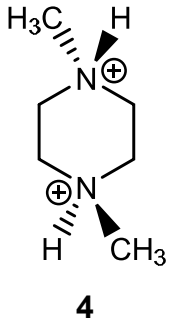
2
MORE BASIC
Is **A** *or* than H_3C-OH ?
LESS BASIC

Rubric: For each acid-base reaction,
3 points for each pair of correctly drawn arrows.
(1 point for just one arrow correct.)
1 point total for the set of 2 arrows if you drew the lines in the correct place, but arrow heads were incorrect.
You can start arrow from a lone pair or from a negative charge sign (if available).
2 points for each acid/base comparison.
2 points for each product. *Structures must be correct; no partial credit.*



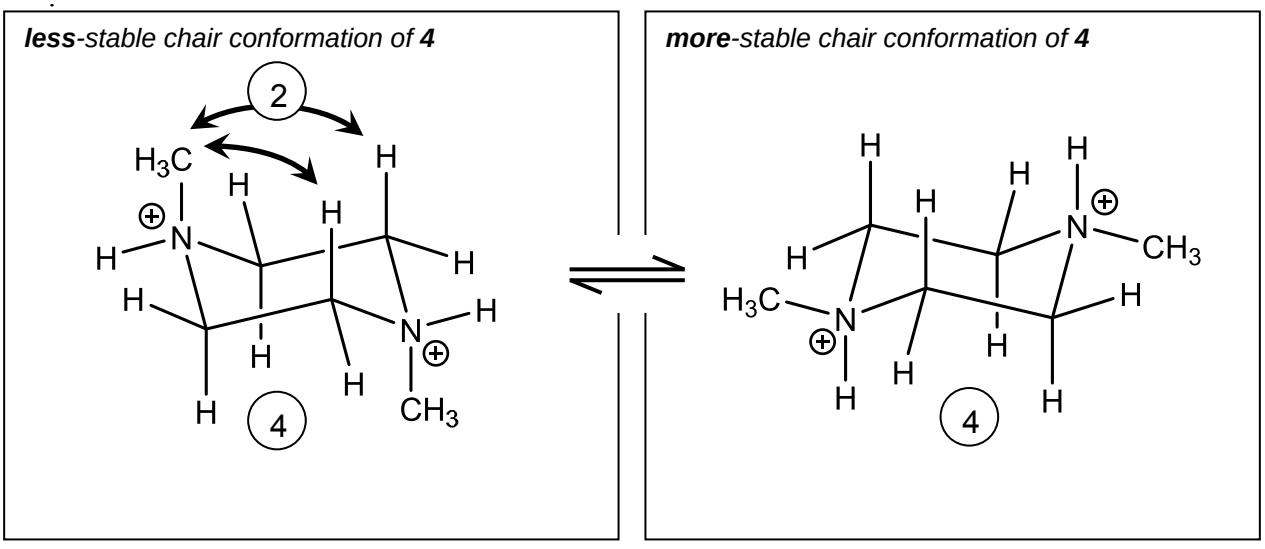


6. (20 pts) The di-cation molecule **4** exists in two equilibrating chair conformations.


4

   a. In the boxes below, draw the less stable chair conformer of molecule **4** on the left, and the more stable one on the right. **Draw every hydrogen attached to the six-membered ring.**

   b. In one of the two conformers, the molecule experiences de-stabilizing 1,3-diaxial (steric) interactions. **Illustrate one of these interactions with a double-headed arrow** on the appropriate conformer.



Rubric for parts (a) and (b):

4 points for each chair.

1 point partial for drawing a chair. Any chair. Must have three pairs of parallel lines.

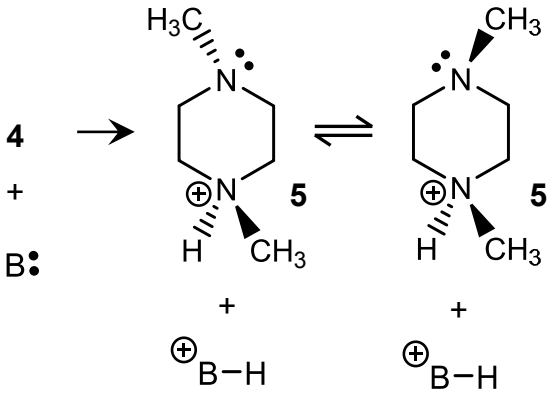
1 point partial for drawing every axial & equatorial hydrogen correctly. Each equatorial C-H bond must be parallel to a ring C-C bond.

2 points for positioning methyl groups correctly. 1 point for each chair either being diaxial or diequatorial. 1 point for putting diaxial as less stable and diequatorial as more stable.

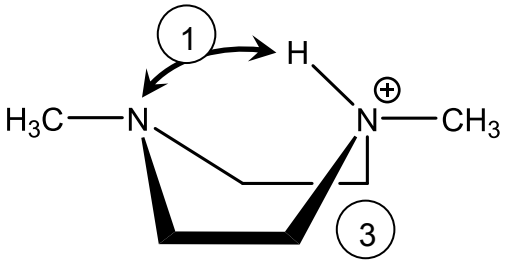
2 points for drawing one double headed arrow for a 1,3-diaxial steric interaction.

c. Are the methyl groups in **4** oriented ***cis-*** or ***trans-*** (2) ? (Circle one.)

d. When molecule **4** is exposed to enough base to remove just one proton, the result is cation **5**, in which one of the methyl groups is free to switch faces: The most stable conformation of **5** is actually not a chair, but a boat. Draw the most stable boat conformation of **5** in the box below. Feel free to omit H atoms attached to carbon.



*most stable boat conformation of **5***



e. The boat conformation of **5** is stabilized by a hydrogen bond. **Illustrate that hydrogen bond with a double-headed arrow** in your drawing on the previous page.

Rubric for parts (d) and (e):

3 points for boat.

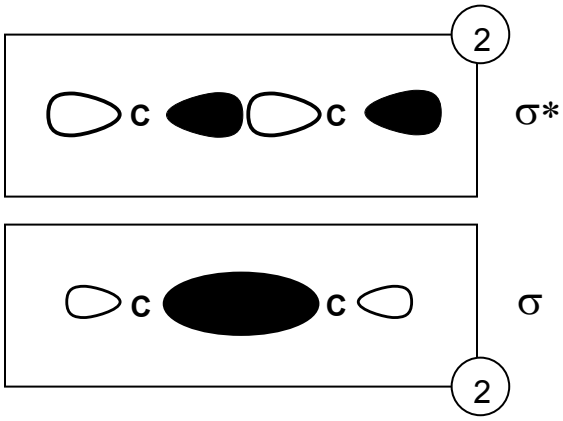
1 point partial for drawing any boat.

1 point partial for positioning nitrogens and methyl groups at tips of boat.

1 point partial for positioning lone N-H in between N's.

1 point for drawing one double headed arrow for hydrogen bond.

f. Both molecules **4** and **5** have 2 C-C bonds; each of these bonds is associated with a σ bonding orbital and a σ* anti-bonding orbital. What do these orbitals look like? In the space on the right, illustrate these two molecular orbitals with lobes, and shade in those lobes according to their phase.



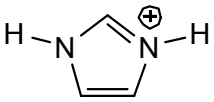
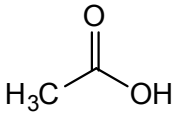
Rubric for part (f):

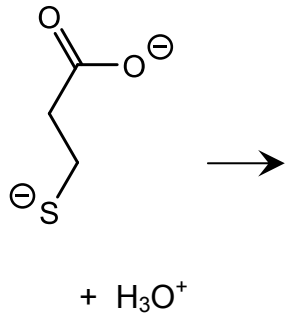
2 points for each orbital.

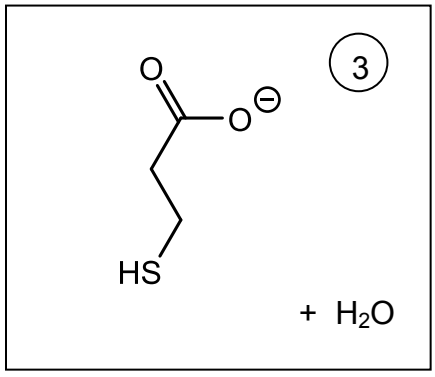
1 point for any σ orbital that has no node in the middle.

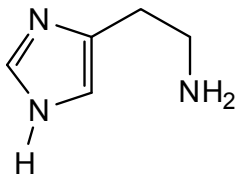
1 point for any σ orbital that has a node in the middle.*

7. (6 pts) Each of the basic molecules below has multiple potential protonation sites. Given the pKa values in the chart on the right, draw the organic product you would expect if each molecule was combined with just one molecule of H_3O^+. Make sure your equation is balanced.

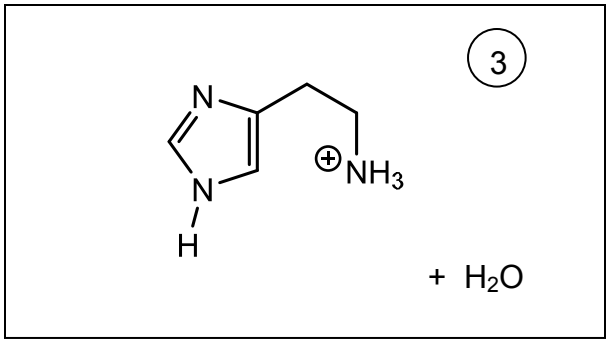
	pK$_a$
$H_3C-\overset{\oplus}{N}H_3$	10.6
H_3C-SH	10.6
	7.0
	4.7







+ H_3O^+ ⟶



Rubric:

3 points for each answer. *No partial credit.*