

Chem 314  
Final Exam  
Spring, 2011  
Beauchamp

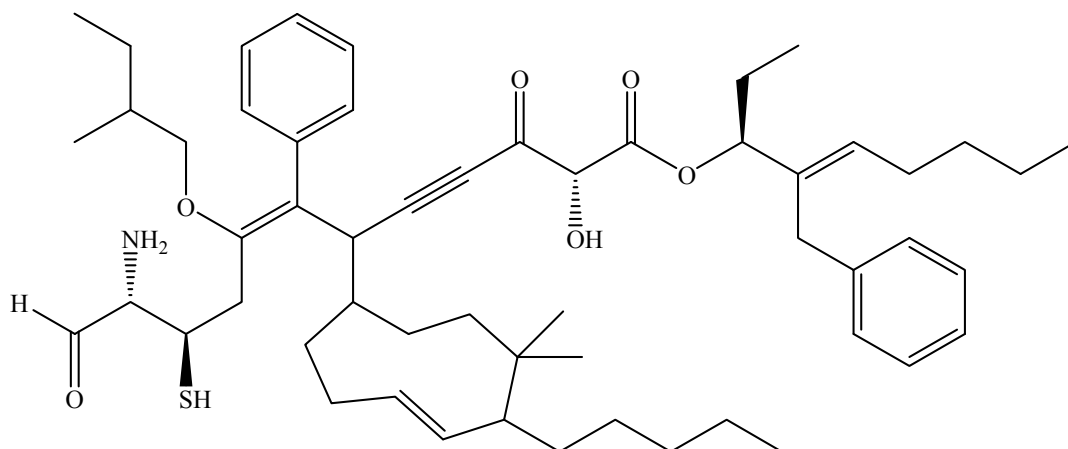
Name \_\_\_\_\_

Problem	Points	Credit
1. Nomenclature (one structure)	30	
2. 2D Lewis structure (large structure with possible formal charge)	20	
3. 3D Structures, Formal Charge, Resonance, Curved Arrows, Hybridization	30	
4. Cyclohexanes, Conformations, Configurations, Stereoisomers, Newman Projection	32	
5. Stereochemistry Questions	40	
6. Acid/Base Chemistry (arrow pushing, explanation)	40	
7. S <sub>N</sub> and E mechanisms, including stereochemical details	40	
8. Free Radicals, Predict products provide mechanism	40	
<b>Total</b>	272	

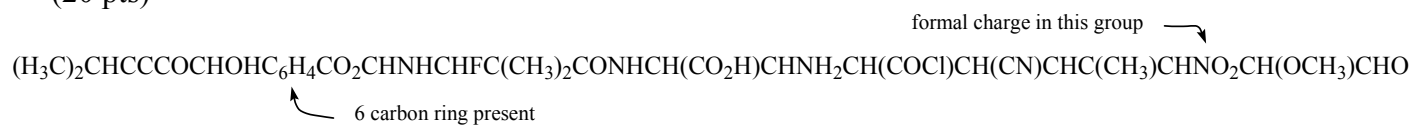
This is a long exam. It has been designed so that no one question will make or break you. You are not expected to completely finish the exam. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement. Do your best to show me what you know in the time available.

A person who wants to do something will find a way, a person who doesn't will find an excuse.  
Stephen Dolley

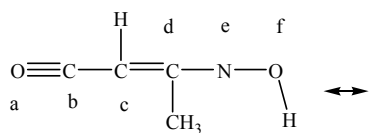
1. Provide an acceptable name for the following structure. Indicate the absolute configuration of any chiral centers shown in three dimensional form (R/S) and any E/Z stereogenic centers. (30 pts)



2. Draw an acceptable 2D Lewis structure for the following formula. Indicate any formal charges present. (20 pts)



3. First, draw three other 2D resonance structures to delocalize any formal charge present. Include proper curved arrow conventions, including lone pairs and formal charge. Rank your structures from best (= 1) to poorest. Draw a three-dimensional Lewis structure of "A" and the best other resonance structure. Show sigma bonds as lines, wedges and dashes and the 2p orbitals in pi bonds as well as any orbitals holding lone pairs. Draw 2 dots for lone pair and  $\pi$  bond electrons. Use structure A to fill in the table at the bottom. **Assume that all nonhydrogens atoms have full octets, unless a carbocation is written.** (30 pts)



A

B

C

D

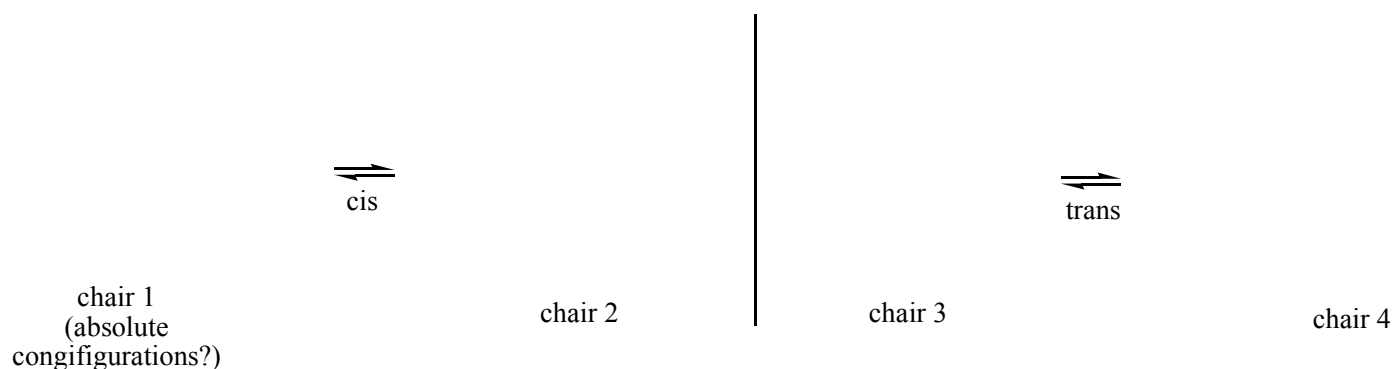
3D (A)

3D (best other)

Use structure A to fill in the following table.

	Hybridization	Angles	Shape	# $\sigma$ bonds	# $\pi$ bonds	# lone pairs
a						
b						
c						
d						
e						
f						

4. a. Draw both chair conformations of trans-1,2-dibromocyclohexane and cis-1,2-dibromocyclohexane. Indicate which conformation is more stable in each pair. Which conformation, overall, is most and least stable? What are the absolute configurations of all stereogenic atoms in chair 1? (20 pts)



most stable (1 or 2) = \_\_\_\_\_

most stable (3 or 4) = \_\_\_\_\_

most stable overall (1,2,3,4) = \_\_\_\_\_

least stable overall (1,2,3,4) = \_\_\_\_\_

stereochemical relationship of 1 with 2? enantiomer, diastereomer, meso, identical, none

stereochemical relationship of 1 with 3? enantiomer, diastereomer, meso, identical, none

stereochemical relationship of 1 with 4? enantiomer, diastereomer, meso, identical, none

stereochemical relationship of 3 with 4? enantiomer, diastereomer, meso, identical, none

- b. Use the most stable conformation from part a and draw a Newman projection using bonds  $C_1 \rightarrow C_2$  and  $C_5 \rightarrow C_4$  for your structure (indicate which chair you are using from part a, (1,2,3,4), and number it appropriately in part a). Point out any gauche relationships in the branches. (4 pts)

Newman projection of the third most stable conformation from part a

- c. Assume an axial Br raises the energy by 1.0 kcal/mole and two gauche Br's raises the energy by 0.5. Use these energies to estimate an relative energy for each of the conformations in part a (1,2,3,4) (8 pts)

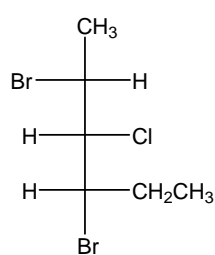
chair 1

chair 2

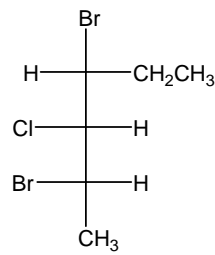
chair 3

chair 4

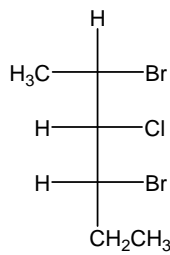
5. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections having the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (18 pts)



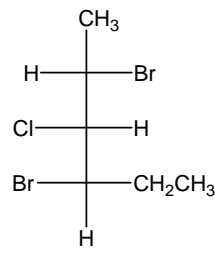
A



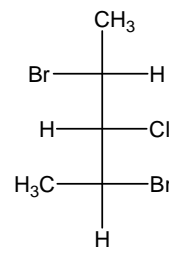
B



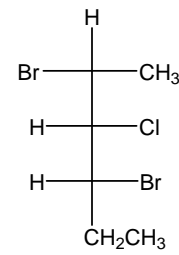
C



D



E



F

- Which are meso?
  - Which is not an isomer with the others?
  - Which pairs are enantiomers?
  - Which pairs are identical?
  - Which pairs are diastereomers?
  - Which would probably rotate plane polarized light (must be a chiral molecule)?
- g. Draw Fischer projections of any stereoisomers of "A" which are not shown above. If there are none, indicate this. (6 pts)

- h. Using isomers of dichlorocyclohexane, draw a pair of diastereomers where at least one of the stereoisomers is chiral, a pair of achiral diastereomers, a pair of enantiomers, an achiral compound that does not have any stereoisomer and a meso compound. (12 pts)

a pair of diastereomers  
where at least one of the  
stereoisomers is chiral

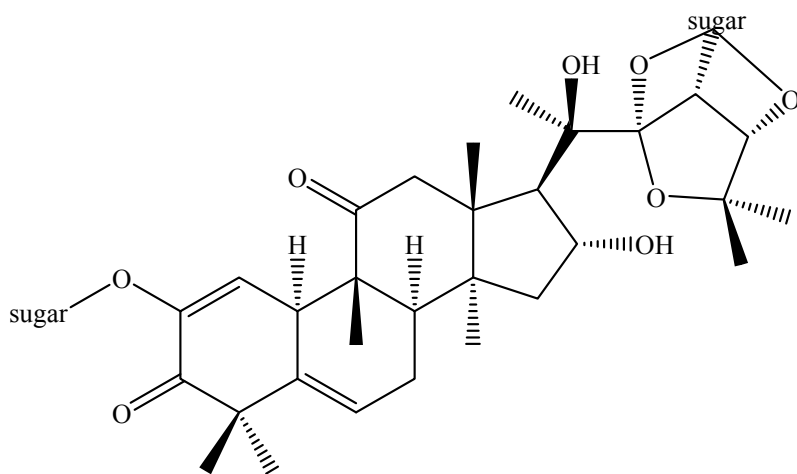
a pair of achiral  
diastereomers

a pair of enantiomers

an achiral compound  
that does not have  
any stereoisomer

a meso compound

- i. The structure of machiluside A was recently determined. It was isolated from the bark of a plant long used for medicinal purposes in China (Org. Lett. p.2856, 2011). Circle all chiral centers and any other stereochemical features in the partial structure below, and calculate the maximum number of stereoisomers possible. (4 pts)

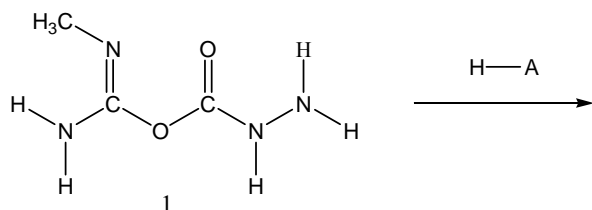


simplified structure of machiluside A  
medicinal plant from China

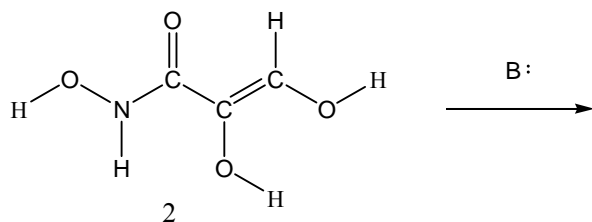
maximum number of  
stereoisomers = \_\_\_\_\_

6. Each molecule below can act as either an acid or a base (they are amphoteric). Use a general acid, HA, and show molecule 1 acting as a base at its most basic site. Use a general base, B:, and show molecule 2 reacting as an acid at its most acidic site. Use curved arrows to show the flow of electrons and include formal charge and lone pairs. Draw all resonance structures important to the conjugate acid or base. Provide a brief explanation for why your "acid" and "base" is the "best" choice. (12 pts each)

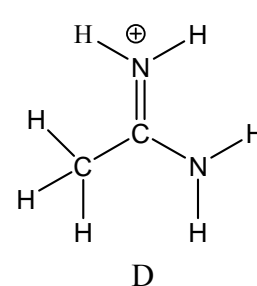
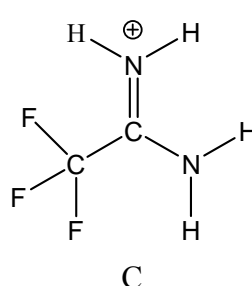
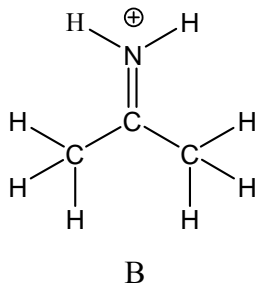
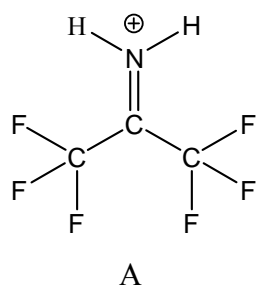
a. reaction in acid, HA



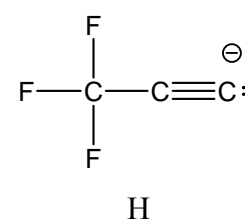
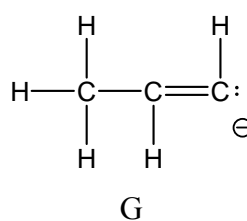
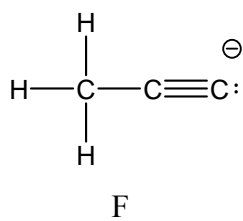
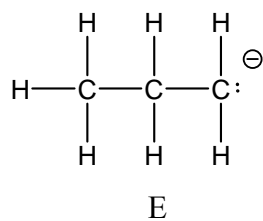
b. reaction in base, B:



c. Order the following structures from strongest acid (=1) to weakest acid. Provide a very brief explanation for your order (this might require additional structures). Show the mechanism for the strongest acid using base, B: (8 pts)



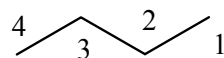
d. Order the following structures from strongest base (=1) to weakest base. Provide a very brief explanation for your order. Show the mechanism for the strongest base using acid, H-A. (8 pts)





7. Use 5S-deuterio-4R-bromo-3R-methylheptane to provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If reactants are not drawn in the proper orientation to show how the reaction must proceed, then redraw them in a more informative way that shows this. **Do not** consider carbocation rearrangement possibilities, since we did not cover them. (39 pts)

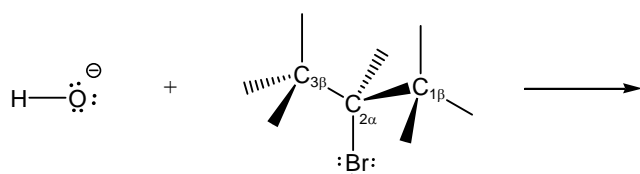
a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (3 pts)



2D structure

3D structure of (1S,2R,3R)-2-bromo-1,3-dideuterio-1-triisobutylbutane

b. Show the  $S_N$  reaction (what kind?), indicate the absolute configuration(s) of the  $C_\alpha$  center in the product. (6 pts)

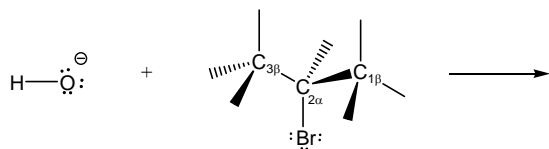


mechanism



$C_\alpha$   
configuration

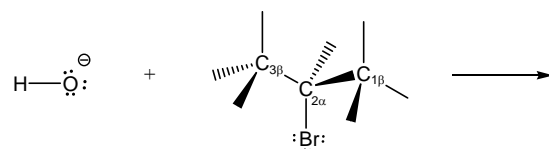
c. Show a mechanism for each  $C_\beta$  position and simply draw all other possible E reaction products (what kind?). Indicate if E, Z or neither. (12 pts)



mechanism



E / Z  
configuration

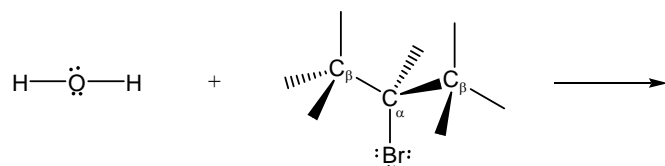


other possible E products



E / Z  
configuration

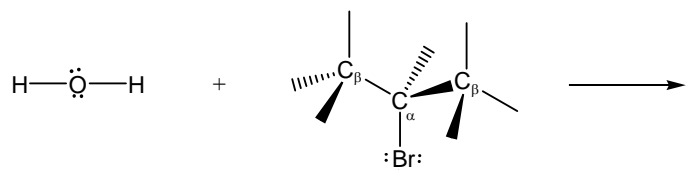
d. For the following examples, use 2S-bromobutane as the R-X compound. Show all steps of the  $S_N$  reaction (what kind?). You can use one intermediate to show all possible  $S_N$  possibilities. Indicate the absolute configuration(s) of the  $C_\alpha$  center in the product. (8 pts)



mechanism

 $C_\alpha$   
configuration(s)

e. Show a mechanism for two E products and all possible E reaction products (you can use the same intermediate). Indicate if E, Z or neither. (11 pts)



mechanism



E or Z

other possible E products

1

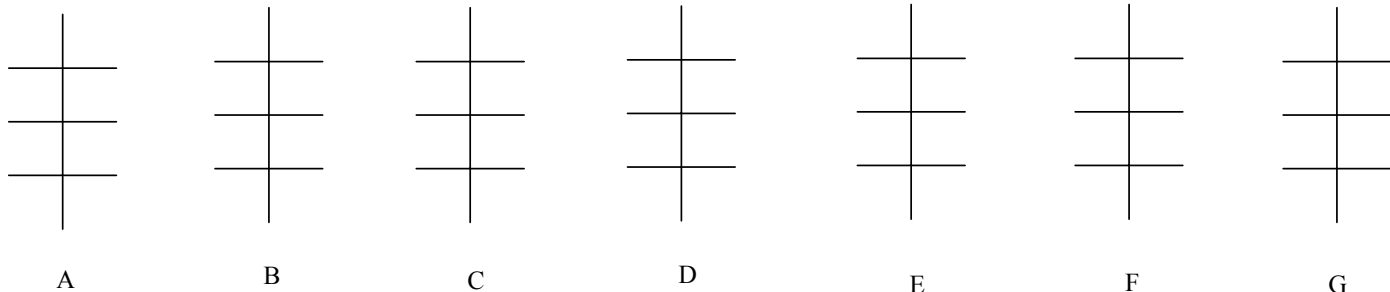
2

3

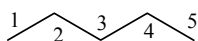
4

5

8. a. Show all possible products when 2S-bromopentane is monobrominated with  $\text{Br}_2/h\nu$ ? Use as many Fischer projection templates as you need. Draw a 3D representation of the starting material. Provide an example of any type of isomerism that is present in the product structures (enantiomers, diastereomers, meso compounds, positional – use your letters). Indicate the approximate relative amounts of each product formed (under the letter) if the relative rates of reaction of a bromine atom with an  $\text{sp}^3$  C-H bond are: primary = 1, secondary = 80, tertiary = 1600, and bromo substituted carbon = 400. (24 pts)



3D structure of starting material



example of:

enantiomers  
diastereomers  
meso compound  
positional

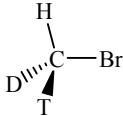
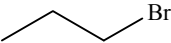
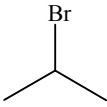
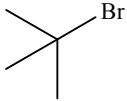

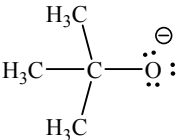
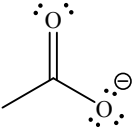


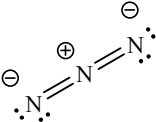
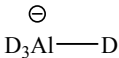
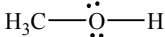
- b. Provide a complete arrow pushing mechanism to explain formation of the major product from the above reaction (show proper curved arrows, lone pairs as two dots and single electrons as one dot). Clearly label each distinct part of the reaction mechanism. Calculate an overall  $\Delta H$  for each step of your mechanism using the given bond energies. (16 pts)

Br—Br	46
H—Br	87
-----	
Me C-H	105
1° C-H	98
2° C-H	95
3° C-H	92
$\text{C}_\alpha$ Br-H	93
-----	
Me C-Br	70
1° C-Br	68
2° C-Br	68
3° C-Br	67
$\text{C}_\alpha$ Br-Br	67

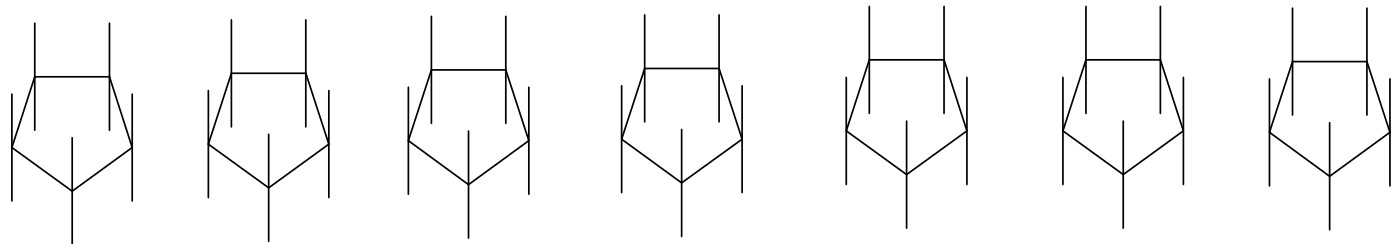
Be curious always! For knowledge will not acquire you; you must acquire it.

9. Fill in the following chart with expected  $S_N/E$  products (show both if formed). Write the appropriate description in each box. (28 pts)

a. only  $S_N2$    b. only E2   c. only  $S_N1$    d. only E1   e.  $S_N2 > E2$    f.  $E2 > S_N2$    g.  $S_N1 > E1$    h.  $E1 > S_N1$    i. no rxn

10. a. Show all possible products when bromocyclopentane is monobrominated with  $\text{Br}_2/h\nu$ ? Use as many Haworth projection templates as you need. Provide an example of any type of isomerism that is present in the product structures (enantiomers, diastereomers, meso compounds, positional – use your letters). Indicate the approximate relative amounts of each product formed (under the letter) if the relative rates of reaction of a bromine atom with an  $\text{sp}^3$  C-H bond are: primary = 1, secondary = 80, tertiary = 1600, and bromo substituted carbon = 1000. (24 pts)



A

B

C

D

E

F

G

example(s) of:

enantiomers

diastereomers

meso compound

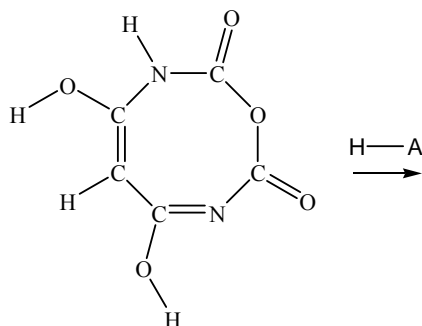
positional

- b. Provide a complete arrow pushing mechanism to explain formation of the major product from the above reaction (show proper curved arrows, lone pairs as two dots and single electrons as one dot). Clearly label each distinct part of the reaction mechanism. Calculate an overall  $\Delta H$  for each step of your mechanism using the given bond energies. (16 pts)

Br—Br	46
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Me C-Br	70
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2° C-Br	68
3° C-Br	67
$\text{C}_\alpha\text{Br-Br}$	67

11. The molecule below can act as either an acid or a base (it is amphiprotic). Use a general acid, HA, to show it acting as a base at its most basic site. Use a general base, B:, to show it reacting as an acid at its most acidic site. Use curved arrows to show the flow of electrons and include formal charge and lone pairs. Draw all resonance structures important to the conjugate acid or base. Provide a brief explanation for why your "acid site" and "base site" is the "best" choice. (12 pts each)

a. reaction in acid, HA



b. reaction in base, B:

