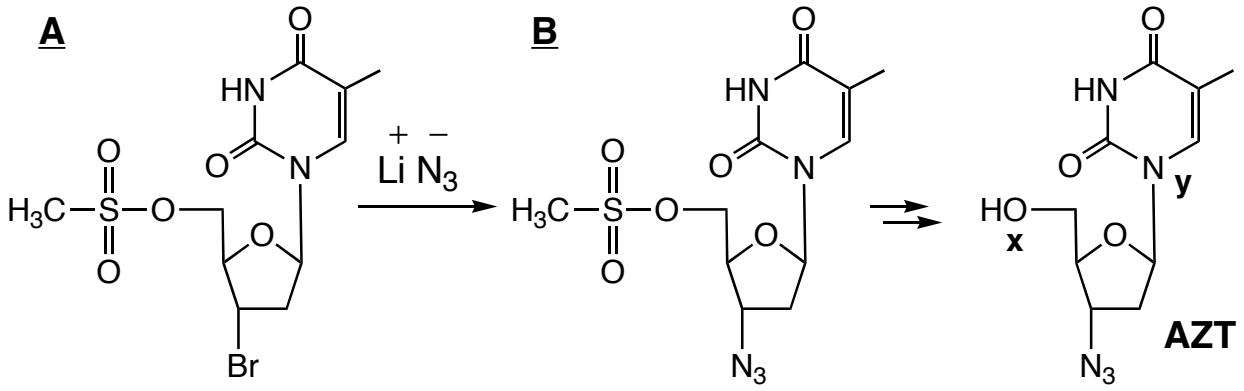
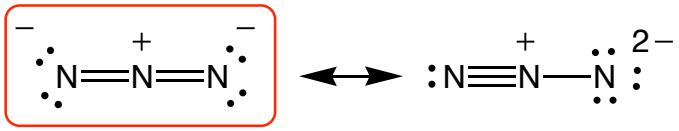
**Prof. Thomas Poon**
**Joint Science Department, The Claremont Colleges**

**A** with azide ion to give **B**. Refer to the scheme below and answer the questions that follow.

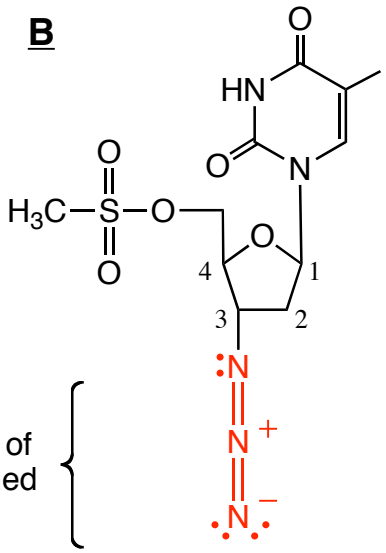



A) In the space below, draw the two most valid resonance structures for the azide ion ($N_3^-$). Circle the major contributor. *Note: for full credit, be sure to show all lone pairs of electrons and charges where appropriate*. (8 points)

The circled resonance structure has more delocalization of charge.



B) Complete the Lewis structure of **B** *after* the azido group has substituted for bromine. *Note: for full credit, be sure to show all lone pairs of electrons and charges where appropriate*. (5 points)




Complete the drawing of the azide group attached to carbon 3.

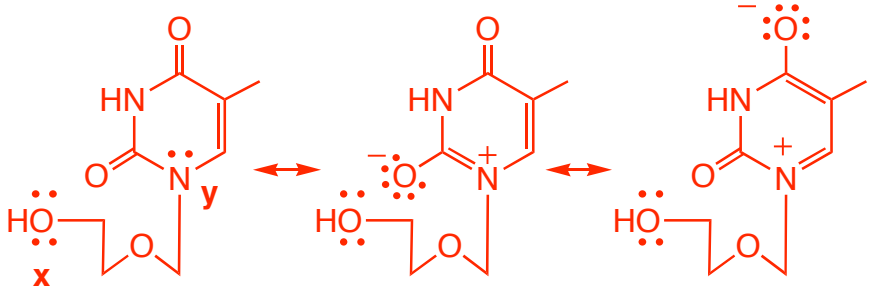
C) What is the overall charge on compound **B**? (2 points)

**zero**

D) Is oxygen, as in ROH, usually more or less basic than nitrogen, as in $RNH_2$? Why? (3 pts)

Nitrogen is usually more basic b/c it is less electronegative and therefore more able to give up its lone pair of electrons.

E) Use pictures & words to explain why oxygen **x** in AZT is more basic than nitrogen **y**. *Note: you only need redraw the relevant parts of AZT, rather than the entire molecule*. (8 points)

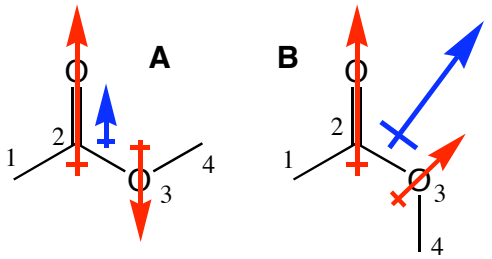


The lone pair of electrons on nitrogen **y** are delocalized via the resonance picture below. This makes them less likely to be donated (i.e. act as a Lewis base).

2) Two possible geometries of methyl acetate are shown below. Suppose you could prevent the free rotation of the bond between atoms 2 & 3. Would you expect the two forms of methyl acetate to have the same or different melting points? If different, which would have the higher m.p.? Explain using pictures & words. (6 points)

**The structure with the largest dipole moment will be the most polar, and should have the higher melting point.**

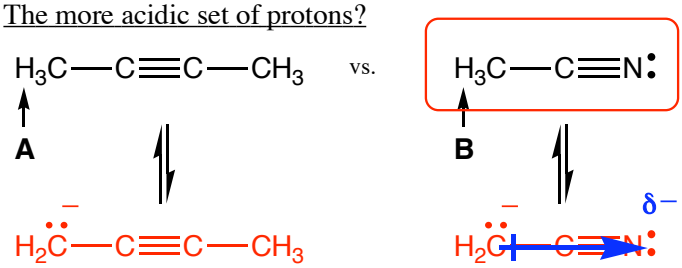
This structure has the oxygens arranged such that their dipoles are oriented in opposite directions, which diminish the overall dipole moment (shown in blue) of the molecule.




This structure has the oxygens arranged such that their dipoles are oriented in the same direction, which increase the overall dipole moment (shown in blue) of the molecule.

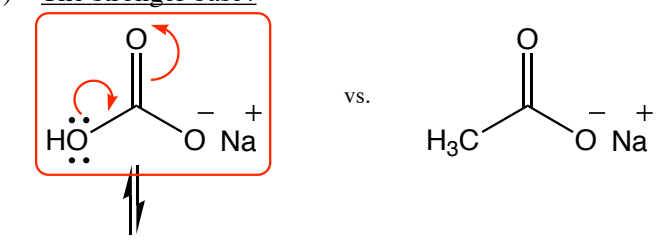
3) For each pair of molecules shown below, select the one that best fits the accompanying description by circling it. Provide a concise but thorough rationale for each of your decisions using words and pictures. *Note: Do not exceed the space provided.* (18 points total)

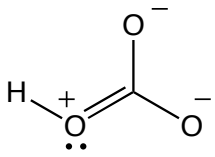
a) The more acidic set of protons?




The nitrogen atom is electronegative and can delocalize the negative charge in the conjugate base via induction. This stabilizes the conj. base, making the original acid more acidic (more likely to give up its proton to form the more stable conj. base).

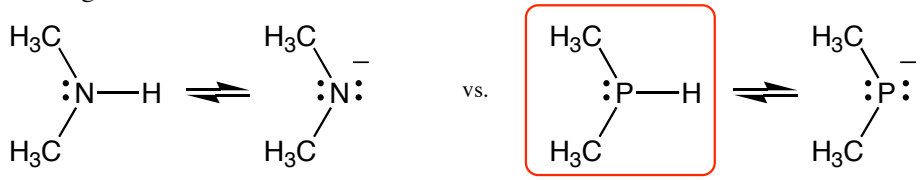
b) The stronger base?



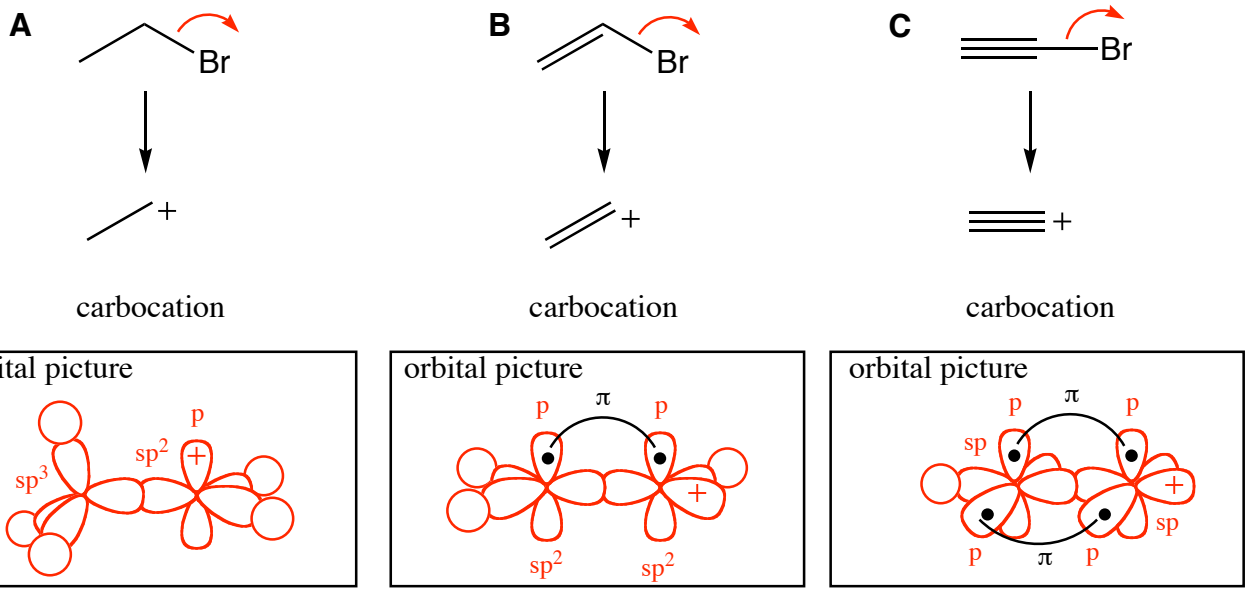
This base has an extra resonance structure that makes both oxygens negative, thus increasing the electron donating ability of the oxygens (or at least statistically making it more likely for the base to react with an acid).

c) The stronger acid?




Phosphorus is larger than nitrogen. Thus, it has a larger electron cloud around it, allowing the negative charge to be more dispersed (delocalized) around the atom. This makes the conjugate base more stable in the phosphorus cmpd than in the nitrogen cmpd., and thus more likely to give up its proton to form the more stable conj. base

4) One possible mechanism of nucleophilic substitution involves the halogen acting as a leaving group to form a carbocation, followed by attack from the nucleophile in a second, separate step. Assume this mechanism is in effect for the following three brominated compounds. Draw Lewis structures for the carbocations that each forms. Then draw an orbital picture for each intermediate in the boxes provided. (9 points)



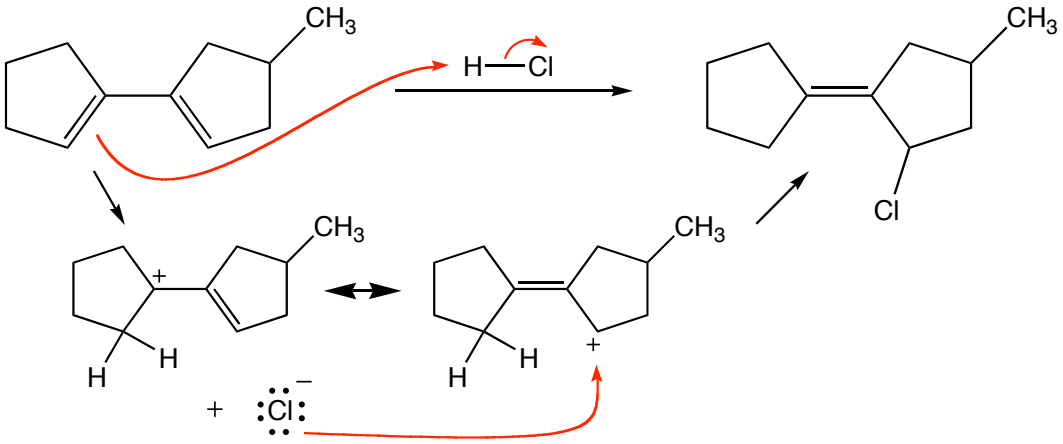

Which compound will undergo substitution the fastest? **A** **B** **C** (circle one, 1 point)

Which compound will undergo substitution the slowest? **A** **B** **C** (circle one, 1 point)

Explain your choices in the space provided. (6 points)

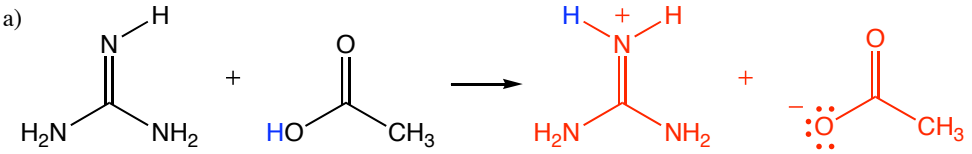
**The electron deficient orbitals are the p, $sp^2$, and sp orbitals for A, B, and C, respectively. The p orbital is the largest and most diffuse of these orbitals, while the sp orbital is the smallest. Recall that when a carbon is negatively charged, it is better to have the electron density brought closer to the nucleus so that the positive charges of the protons in the nucleus can better counterbalance the added electron density. The converse is true in this case, the smaller the orbital, the greater the positive character on the carbon and the less stable it will be. The less stable the intermediate the higher in energy it will be. This will most likely mean that more energy is needed to reach the intermediate, causing a slower reaction.**

5) Using curved arrows, provide a mechanism that explains the following transformation. For full credit, be sure to show the products of each step and indicate formal charges throughout. (8 points)

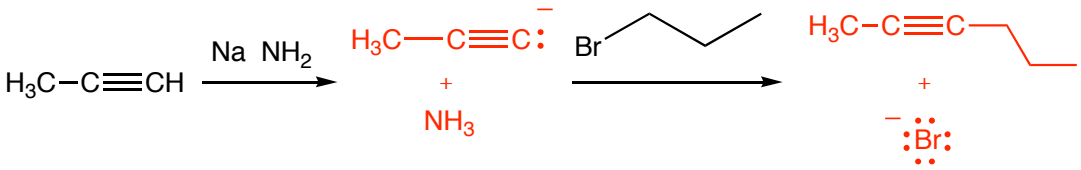


6) Predict the major product(s) of the following reactions. For full credit, be sure to indicate any nonzero formal charges. (15 points)

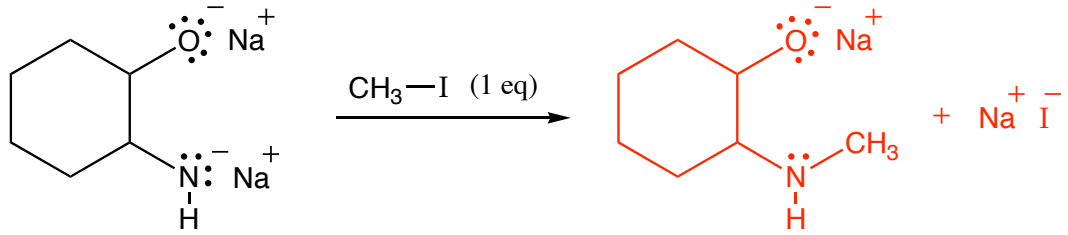
a)



b)

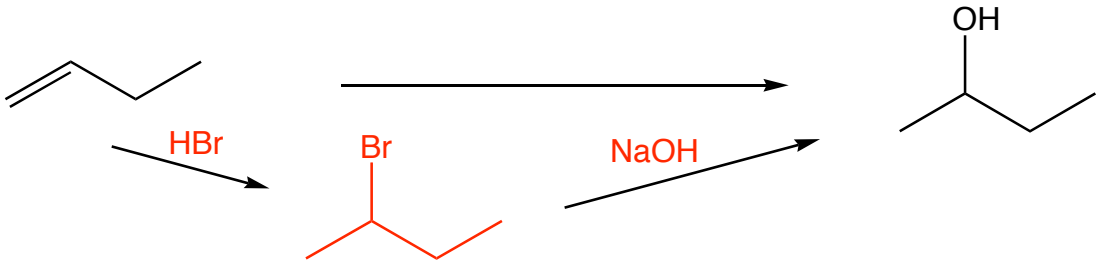



c)

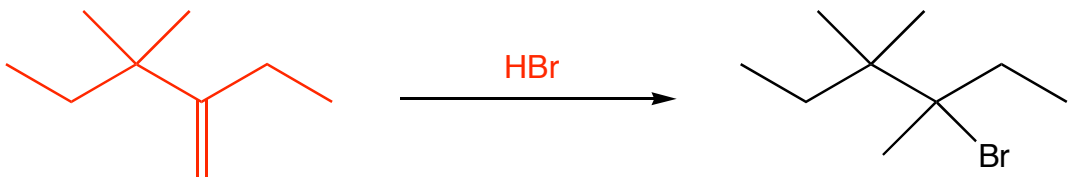



7) Provide syntheses that will accomplish the following transformations. If a synthesis requires more than one step, show the products of each step. (10 points)

a)




b)




any hydrocarbon