Chem 112A: First Midterm

September 25th, 2012

Please provide all answers in the space provided. You are not allowed to use a calculator for this exam, but you may use (previously disassembled) molecular model kits. Including the title page, there should be 7 total questions spread over **10** pages. There is also an eleventh page that should be blank. You can use this last page for scratch paper if you need it, but please remember to copy your answers into appropriate exam question.

Name: Answer Key

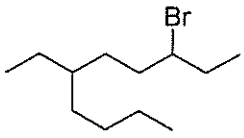
GSI/Section: _____

Question	Points
1	_____ (18)
2	_____ (12)
3	_____ (15)
4	_____ (12)
5a-c	_____ (13)
5d-g	_____ (11)
6	_____ (12)
7a-c	_____ (23)
7d-f	_____ (9)
TOTAL	_____ (125)

1. Nomenclature

Provide an accurate chemical name for the following compound (2 pt)

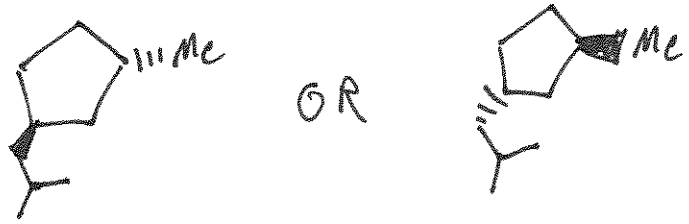
a.



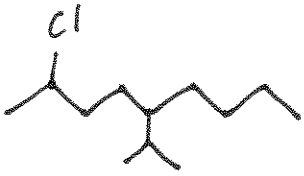
3-bromo-6-ethyldecane

Provide clear structures of each of the following compounds (2 pt each)

b. *trans*-1-isobutyl-3-methylcyclopentane

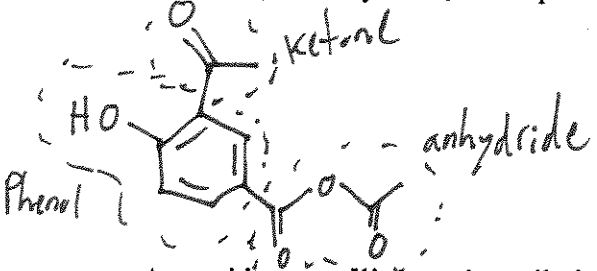


c. 2-chloro-5-isopropylnonane

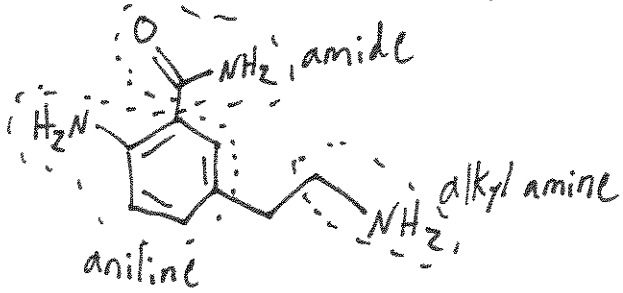


Draw an example of an organic molecule that contains all of the functional groups listed. Circle and label each functional group. (2 pt per functional group)

d. A ketone, an anhydride, and a phenol.

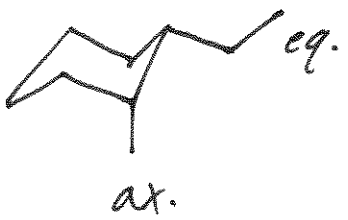


e. An amide, an aniline, and an alkyl amine.

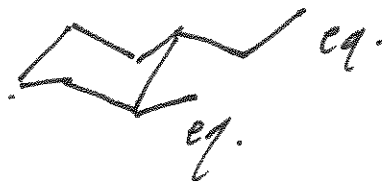


2. Draw pictures to match the following instructions: (3 pt each)

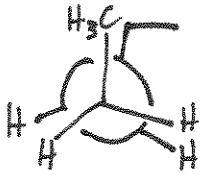
   a. The lowest-energy conformation of *cis*-1-ethyl-2-methyl cyclohexane



   b. The lowest-energy conformation of *trans*-1-ethyl-2-methyl cyclohexane

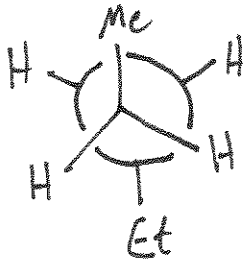


   c. A Newman projection of the C2-C3 bond of pentane in its highest energy conformation



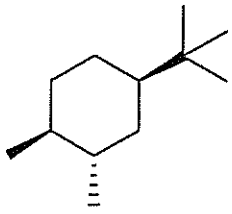
eclipsed Me/Et

   d. A Newman projection of the C2-C3 bond of pentane in its lowest energy conformation



anti Me/Et

3. Conformational analysis of a substituted cyclohexane.



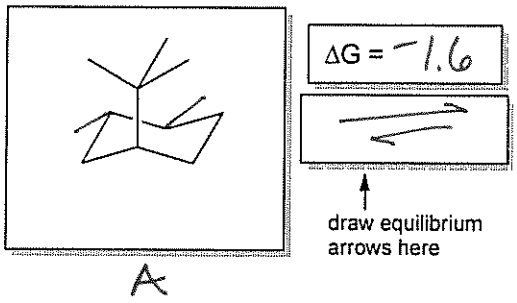
Difference in free energy between axial and equatorial positions on cyclohexane (kcal/mol):

H	0
Me	1.7
Et	1.75
iPr	2.2
tBu	5.0

a. Complete the chair conformation drawings of the above trisubstituted cyclohexane by adding the methyl substituents at the appropriate positions. (4 pt)

b. Using the information provided in the table above, calculate ΔG for this equilibrium. Clearly show your work in the appropriately labeled box. Place your answer in the box labeled ΔG = (2 pt)

c. Based on your calculated ΔG, use equilibrium arrows to express which side is favored. (2 pt)



Show your work for calculating ΔG here

Me → 1.7 × 2 = 3.4

tBu → 5.0

3.4
−5.0
= 1.6 kcal/mol

d. Estimate the equilibrium ratio (major:minor) that the ΔG that you calculated above would correspond to at room temperature. Fill in the blanks below to indicate the order of magnitude. (3 pt)

Between 10 :1 and 100 :1

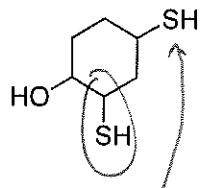
e. What extra interaction(s) between substituents does your calculation neglect? Predict the effect on ΔG (increase or decrease) of each additional interaction(s). (4 pt)

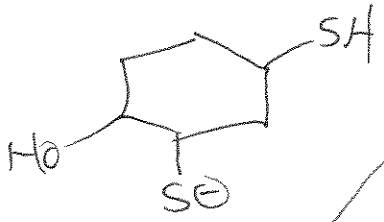
gauche interaction of 1,2 dimethyl makes chair A even more unfavorable, therefore magnitude of ΔG increases, or becomes more negative

4. Acidity and Basicity

Identify the **most acidic site** in each of the following molecules by **drawing the conjugate base.** Briefly *(15 words or less)* explain why you chose that site **instead of the next most acidic site.** (4 pt each)

a.



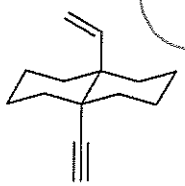


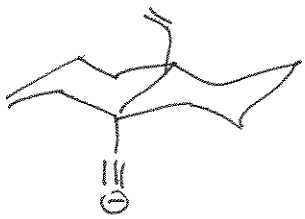
next most acidic site

(same reason as halide acidity trend)

Sulfur more polarizable than Oxygen (/has weaker bond strength with H) and / the indicated Sulfur is more acidic because of 1) inductive effects or 2) hydrogen bonding of anion with ↳OH

b.

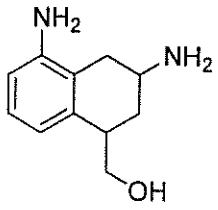


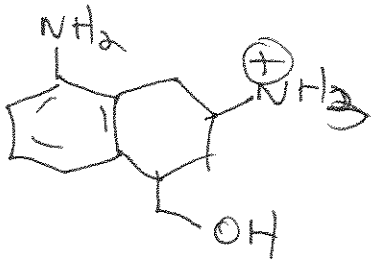


Alkyne carbon is sp vs. sp^2 → more s character ⇒ more electronegative ⇒ better anion stabilization

Identify the **most basic site** in the following molecule by **drawing the conjugate acid.** Briefly *(15 words or less)* explain why you chose that site **instead of the next most basic site.** (4 pt)

c.



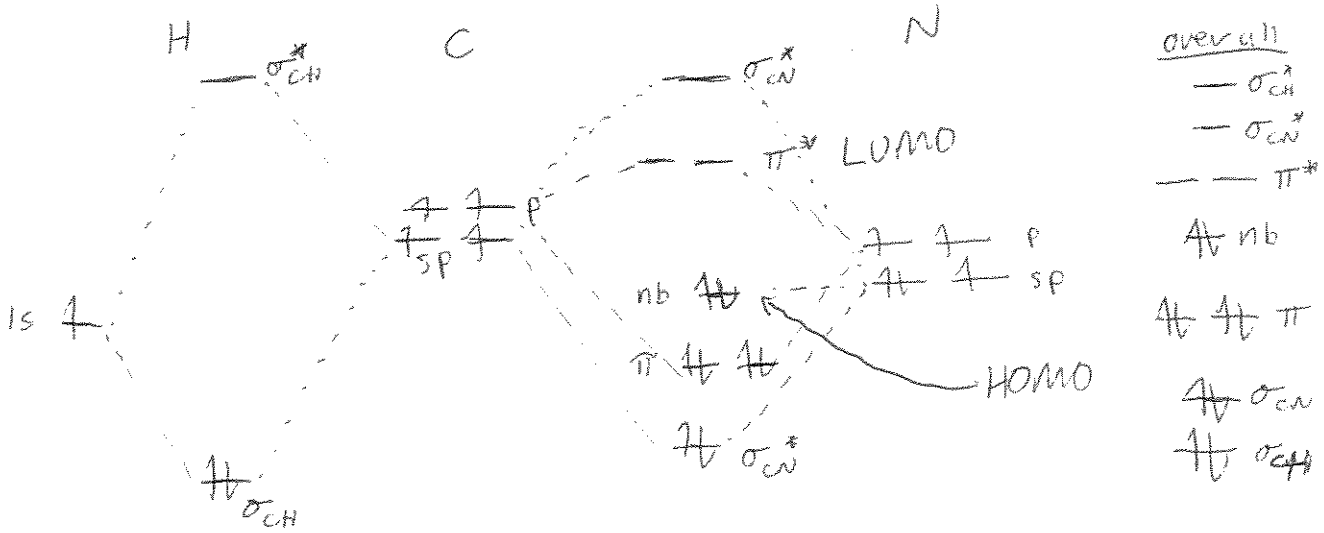


N is less electronegative than O, aniline less acidic than alkyl amine b/c of resonance stabilization in base that is lost in conj. acid.

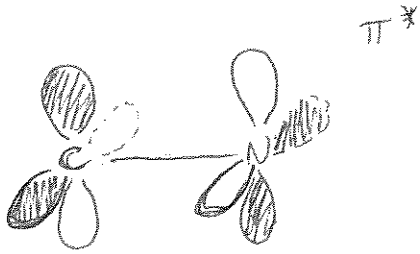
5. Hydrogen cyanide, HCN, is a poisonous compound which has been used as a chemical warfare agent. Its toxicity is caused by inhibition of an enzyme crucial to cellular respiration. HCN is also a feedstock (starting material) for the synthesis of a variety of useful organic compounds.

   a. Draw the **Lewis structure** of HCN, and indicate the **hybridization** of each atom (3 pt).

   b. Construct a molecular orbital diagram for HCN. Make sure that each of your orbitals is labeled (hybridization of atomic orbitals, type of bonding orbital, nonbonding, etc). Fill in the electrons in the MO energy levels, and label the HOMO and LUMO. (6 pt)



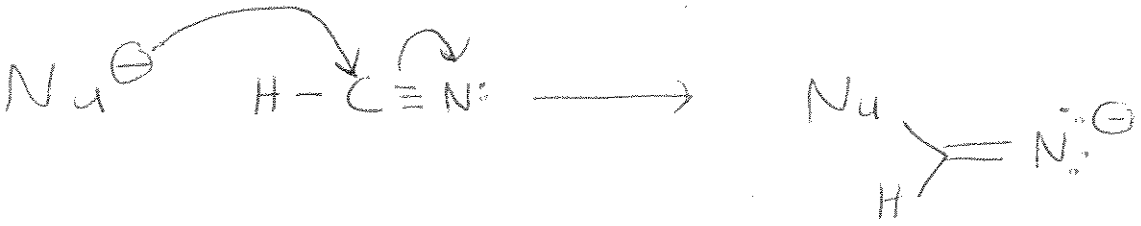
   c. Draw a **three-dimensional** sketch of the LUMO(s), including orbital shading. Include the positions of all atoms in your sketch. (4 pt)



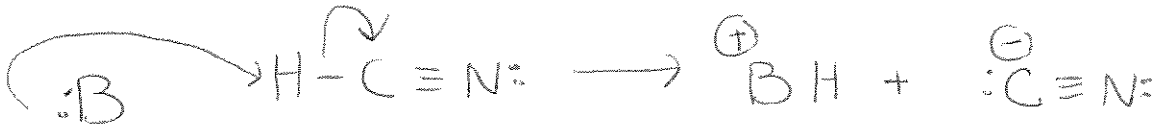
d. If HCN reacted with a nucleophile, what orbital(s) would be involved? (2 pt)

The LUMO of HCN, or $\pi^*_{C\equiv N}$

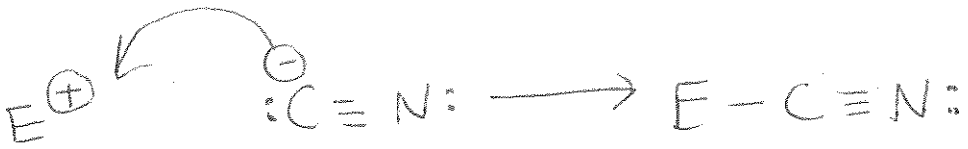
e. Draw a mechanism (curved arrows and product(s)) showing the reaction of HCN with a generic anionic nucleophile (Nu^-). (3 points)



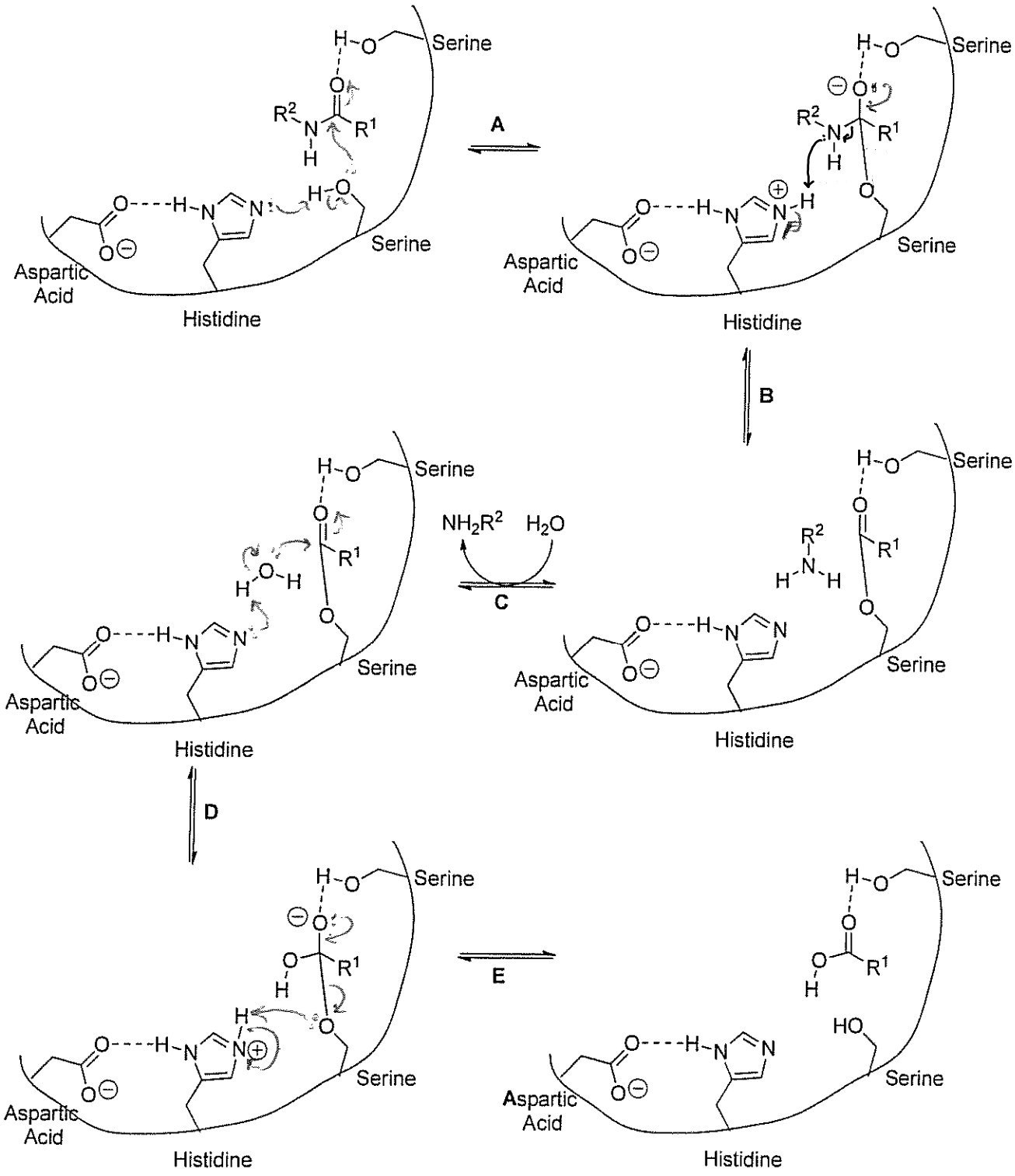
f. HCN could instead react with a base to form a different product. Draw a mechanism (curved arrows and product(s)) showing the reaction of HCN with a generic neutral Brönsted base (B:). (3 points)



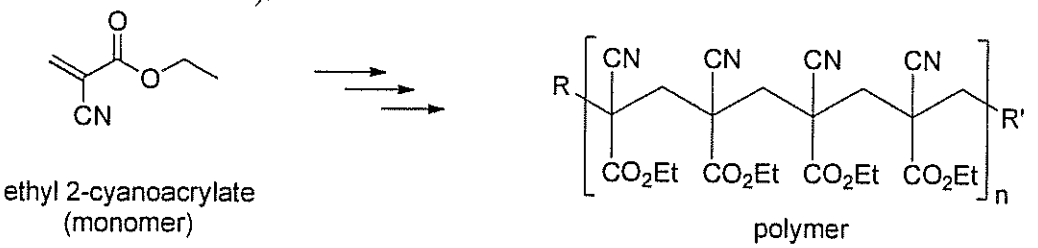
g. Draw a mechanism (curved arrows and product(s)) showing the reaction of the conjugate base of HCN with a generic electrophile (E^+). (3 points)



6. Add curved arrows to steps **A**, **B**, **D**, and **E** in this mechanism to show how amides are converted to carboxylic acids and amines by enzymes. **No curved arrows are required for step C.** *Note: there are hydrogen bonding interactions indicated by dotted lines. These interactions help to organize the positions of the reactants.* (12 pt)



7. Ethyl-2-cyanoacrylate is the active ingredient in Super Glue and Krazy Glue. It acts as an adhesive by rapidly polymerizing upon exposure to a small amount of a nucleophile such as water (moisture from the air).



ethyl 2-cyanoacrylate (monomer)

polymer

a. What three functional groups does ethyl-2-cyanoacrylate contain? (6 pt)

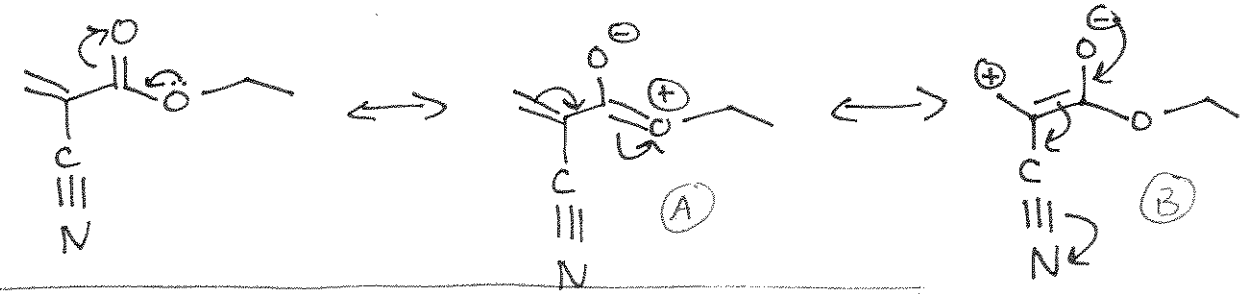
3 pts

Ester, Alkene, Nitrile

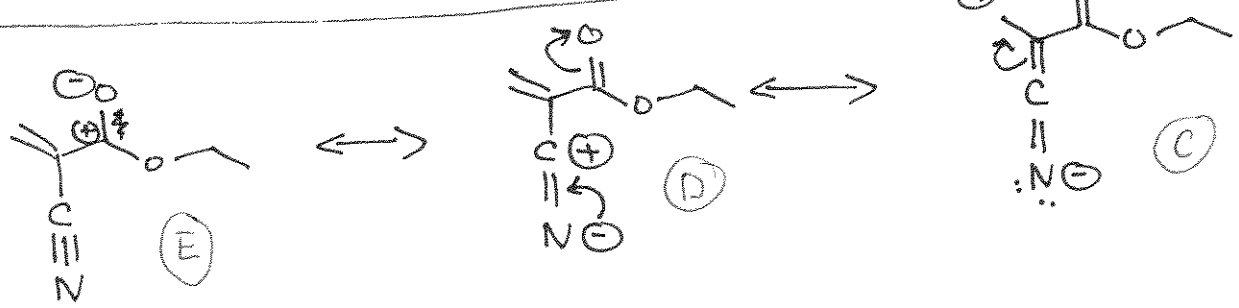
b. Which functional group from the monomer is not present in the polymer? (2 pt)

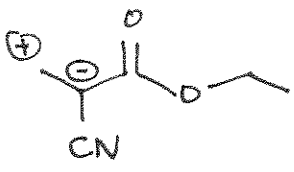
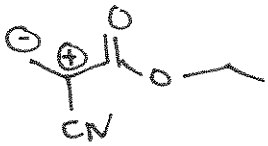
Alkene

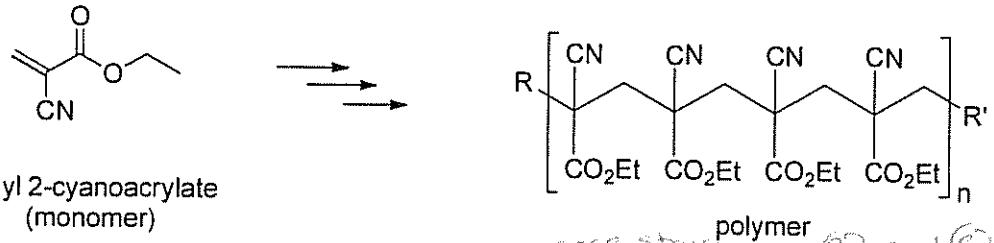
c. Draw five additional reasonable resonance structures of the monomer. Be sure to include all formal charges. Draw curved (electron-pushing) arrows to show how each new resonance structure can be derived from either the structure provided above or from a previous resonance structure. (15 pt)



Structures with more than (2) formal charges or with empty orbitals on O/N were not accepted, as per "rules" outlined in class/homework



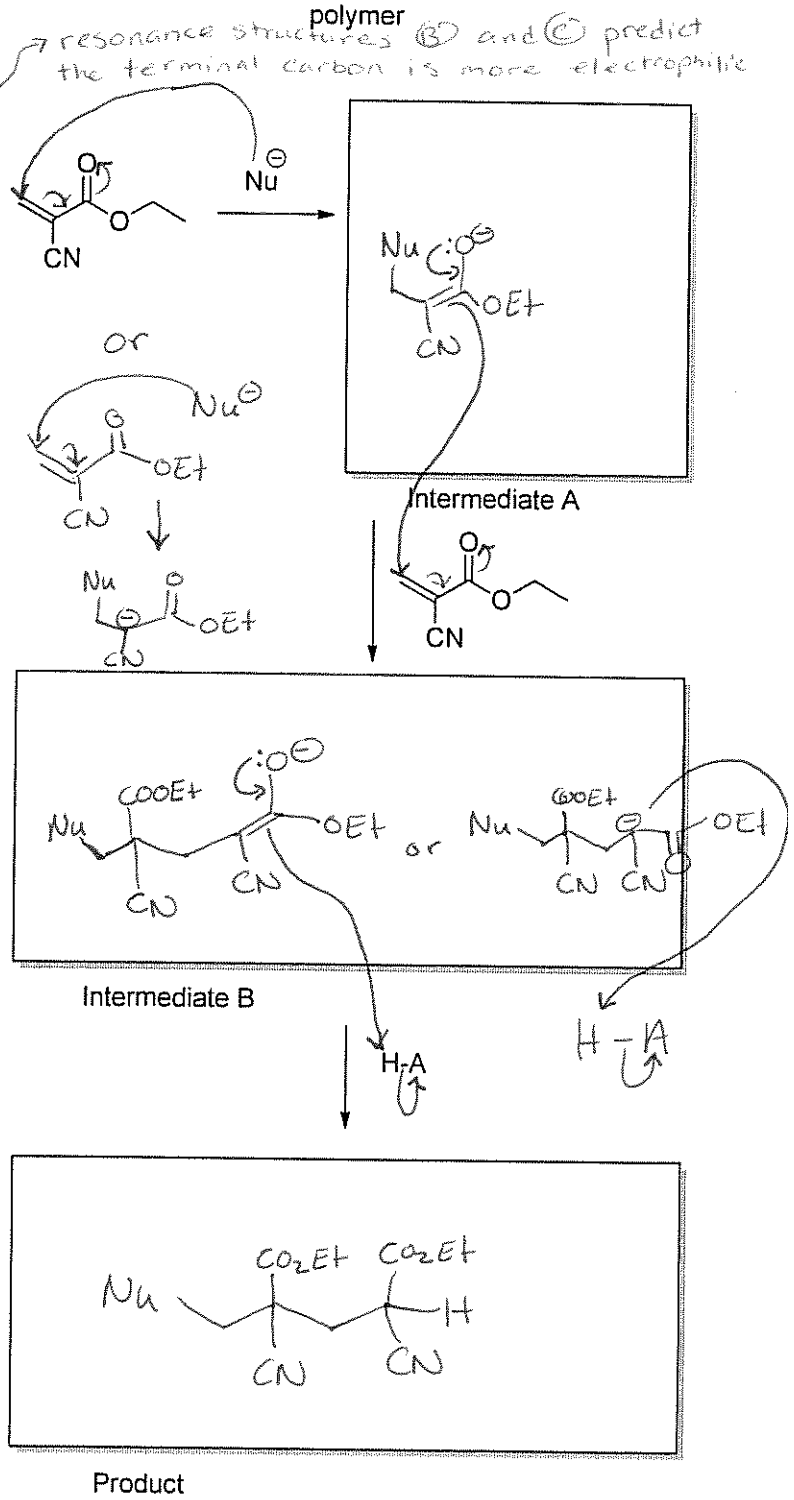
Also accepted:  and 



d. Based on the resonance structures you drew for part c, decide which of the two alkene carbons is more electrophilic, and then **add curved arrows** to the structures provided on the right showing the reaction of a generic nucleophile (Nu^-) with the monomer, then **draw intermediate A**. (3 pt)

e. Intermediate A can be used as a nucleophile to attack a second monomer, which can then attack a third monomer, etc. **Draw curved arrows and a reasonable resonance structure of Intermediate B** for the next step of the reaction in the space provided. Check to make sure that this intermediate corresponds to the desired polymer structure. (3 pt) *(Note: There is more than one possible resonance structure, you only need to show one of them)*

f. After any step, the reaction can be terminated by reaction of an intermediate with an acid. **Draw a curved arrow mechanism and the product** generated by the reaction of intermediate B with a generic acid, H-A. (3 pt)



This last page should be blank. You may use it as scratch paper, but be sure to recopy your answers into the exam questions so that we can grade them easily.