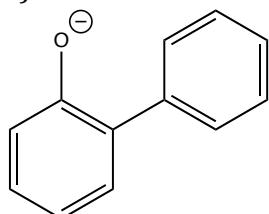


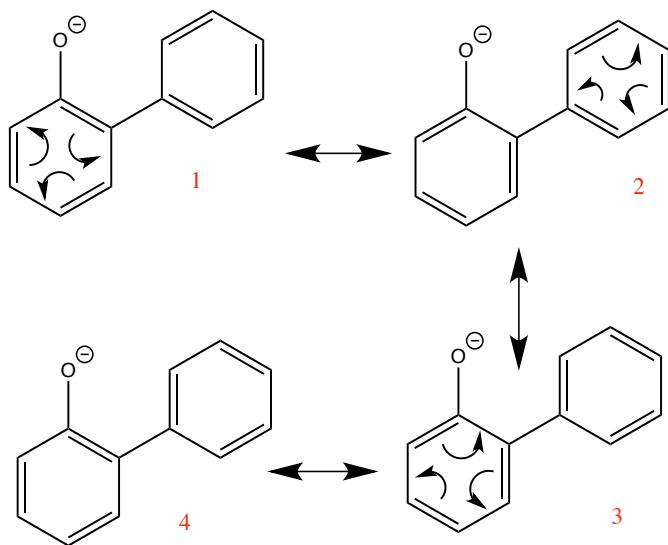
1) Draw all contributing resonance structures with the maximum number of complete octets and the minimum number of atoms with a formal charge. Circle the most contributing resonance structure.

a)



There are a lot of resonance structures for this molecule. I counted thirteen- I'll leave a number next to each unique resonance structure.

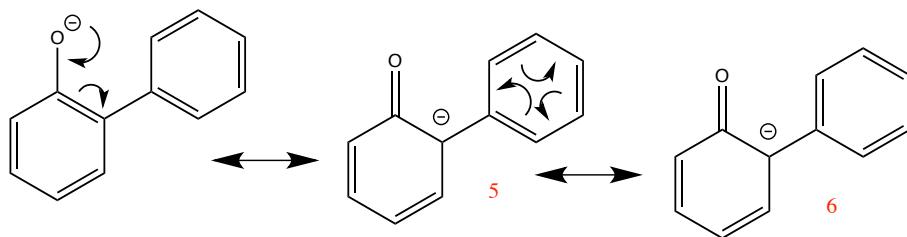
The first thing we have to understand about this molecule is that each benzene ring has an equivalent structure, created by swapping the three double bonds and the three single bonds in the ring.



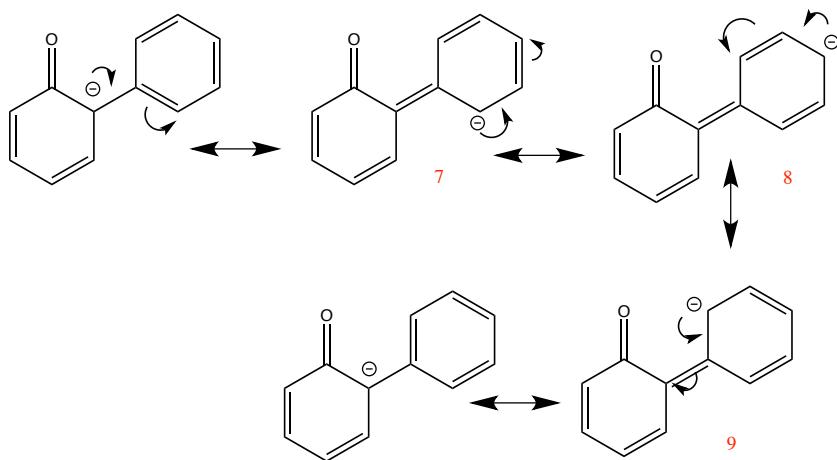
Notice that we used a pi bond as our electron source (we usually use lone pairs as electron sources) and we moved three pairs of electrons at once (we usually only push two). If we tried moving the electrons around the way we usually do, we'd find a lot of intermediates with incomplete octets and wacky formal charges.

I will continue to show benzene resonance structures by pushing all three bonds at once- understand that this is only done for benzene to show the two equivalent ring structures that can be drawn.

Let's start by finding the electron source, usually a free lone pair. In this molecule, we only have one electron source — the negative oxygen atom — and only one bond onto which we can move the lone pair. Once again, the benzene ring can be drawn a different way to show another CRS.

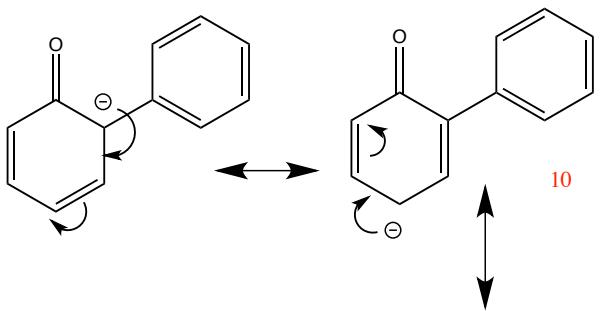


Now, we have two choices of where to move the free lone pair on the negative carbon. We could continue moving it around the left benzene ring (and we'll do that soon enough), but it's important to realize that we can also move it around the right benzene ring.

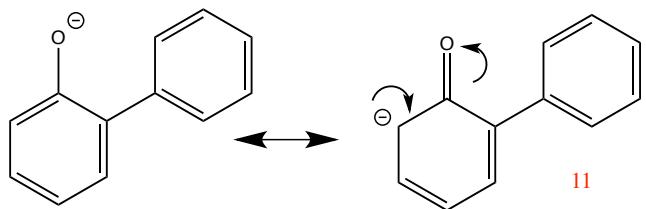


We've already drawn the last resonance structure (see structure 6) before.

To finish up the rest of the resonance structures, we just need to let the lone pair dance around the left benzene ring.

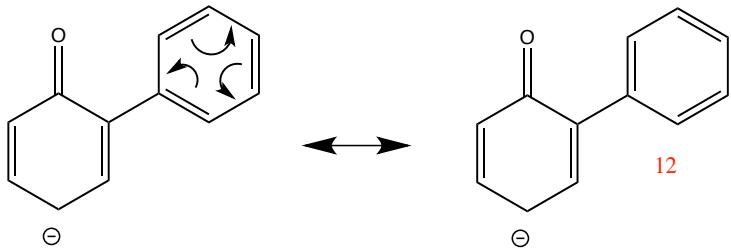


10

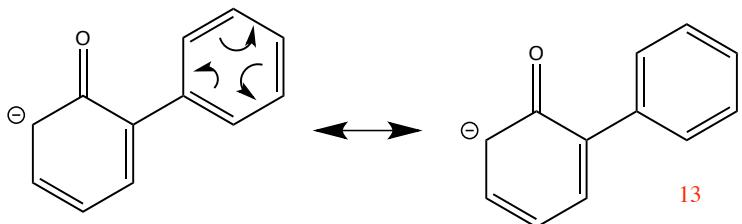


11

Are we done? Almost! I promised thirteen resonance structures- look closely at structures 10 and 11. There is another equivalent resonance structure to draw, one where we flip the single and double bonds in the right benzene ring.



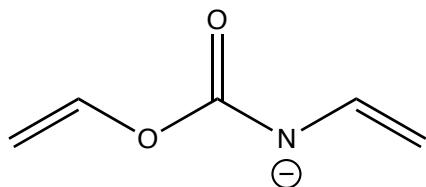
12



13

One last part to this question- which CRSs are most contributing? As always, the negative formal charge is most stable on electronegative atoms. In this case, structures 1-4 are all the most contributing resonance structures, since they have the negative formal charge on the oxygen.

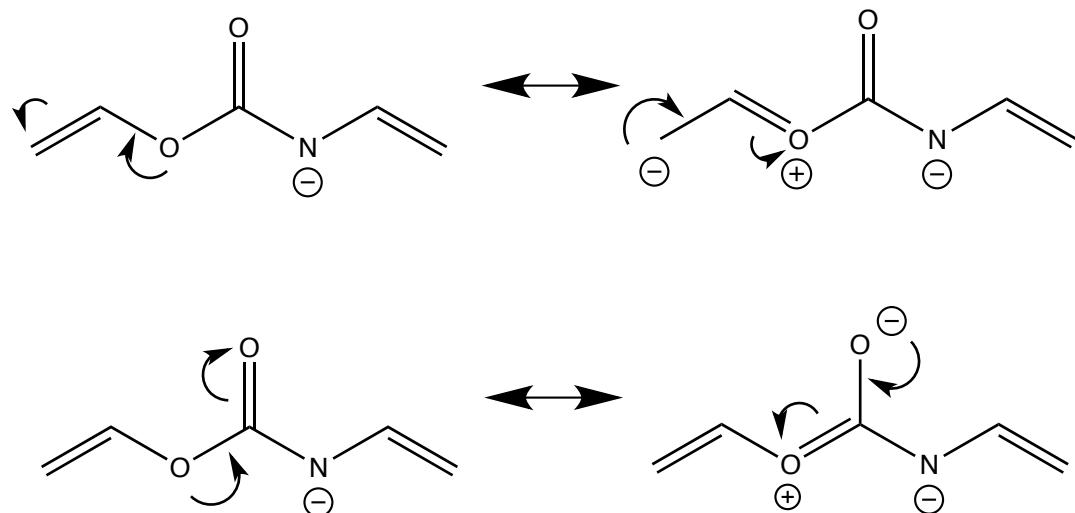
b)



Let's start this problem by considering our electron sources. Unlike the last problem, we have several sources of electrons. Both oxygen atoms and the nitrogen atom have lone pairs that we can push around with resonance.

Before drawing any resonance structures, let's try to narrow down our electron sources. Carbonyl groups are generally poor sources of electrons, and this molecule is no exception- if we tried to push a lone pair from the carbonyl down to form a triple bond, we'd be left with a carbon violating the octet rule. There are no other pi bonds to break to fix this, so we can't make a contributing resonance structure this way.

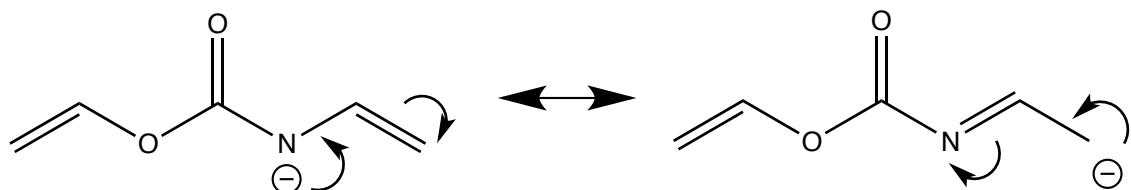
Let's look at the other oxygen. This oxygen actually has a couple options when it comes to resonance. If its lone pair drops to the left, we can push the adjacent pi bond onto the terminal carbon. If its lone pair drops to the right, we can push the adjacent carbonyl bond onto the oxygen.



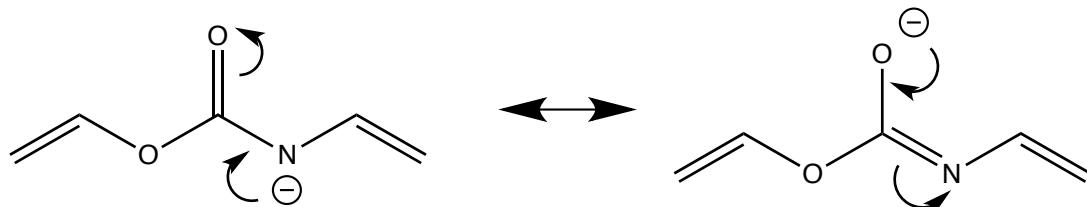
Both of these are valid resonance structures, but their contributions are marginal. More importantly, the question is only asking for resonance structures with a single formal charge, and both of these resonance structures have three. Because of this, we can't make any good resonance structures with the left oxygen. Remember- this oxygen is still sp² hybridized since the resonance structures still exist, even though they aren't necessary for the solution to this problem.

We started with three sources of electrons, but now we're down to only one- the nitrogen. There are only two directions that we can move nitrogen's lone pair: to the left or to the right.

Let's start by moving the lone pair to the right. Once we've pushed the pi bond electrons onto the terminal atom, there isn't really any more resonance that we can draw without going backwards. Recall that moving the lone pairs on the oxygen atoms did not produce good resonance structures.



Now that we're done moving the lone pair to the right, let's go back to our original structure. Recall that we can also move the lone pair to the left. There's only one pi bond that we can rearrange, so let's move two carbonyl electrons onto the oxygen.



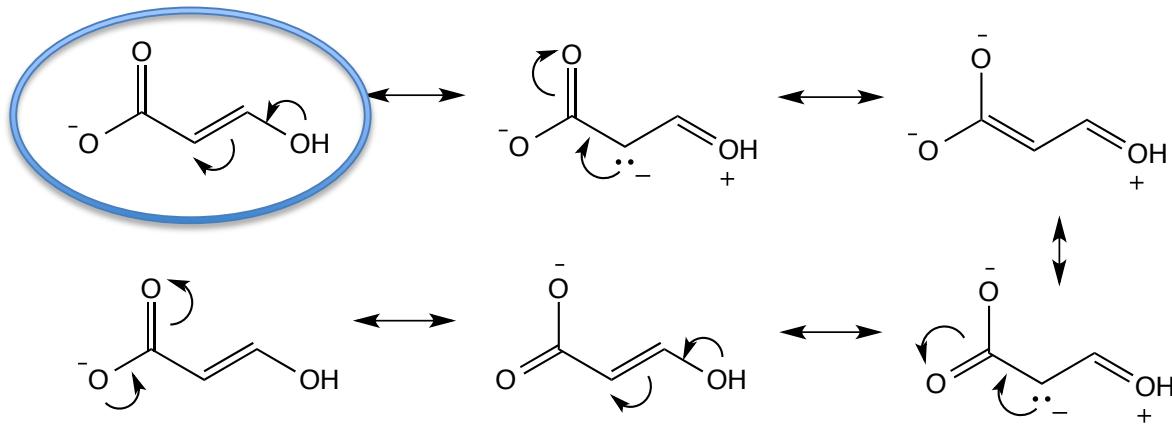
Earlier, we said that this carbonyl oxygen was a poor electron source and didn't make good resonance structures, and yet we're making a resonance structure with it now. This carbonyl group is a poor *source* of electrons, but in this structure, the source of electrons came from the nitrogen. The carbonyl is instead acting as an effective electron sink.

Same as before, we can't move any further with resonance structures without tracing back our steps. Despite all of the pi bonds and lone pairs, this molecule only has three major resonance structures.

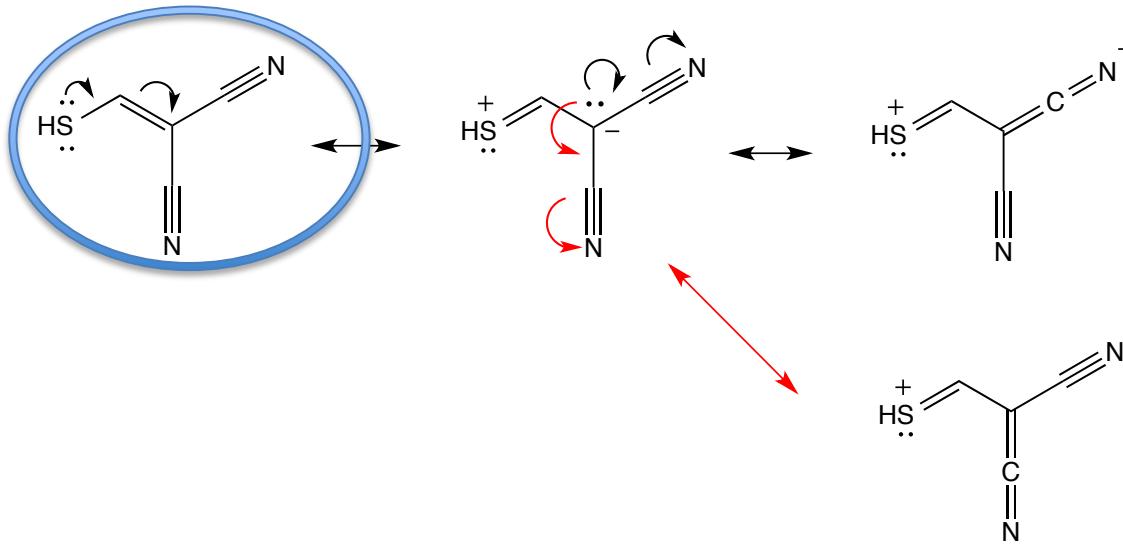
We can figure out which of these three is the most contributing structure in the same way that we did last problem- prefer resonance structures where the negative formal charge is on the most electronegative atom. In our three resonance structures, we have one each of a negative charge on a carbon atom, a nitrogen atom, and an oxygen atom. Since oxygen is the most electronegative of the three, the resonance structure where oxygen has a negative charge (the last one drawn) is the most contributing.

2. Draw all contributing resonance structures with the maximum number of complete octets. Circle the most contributing resonance structure.

- a) Remember: switching the bonds in the carboxyl group gives us an additional two resonance structures. All resonance structures have full octets, but one the original structure minimizes formal charge. Therefore, the starting structure is the most contributing resonance structure.

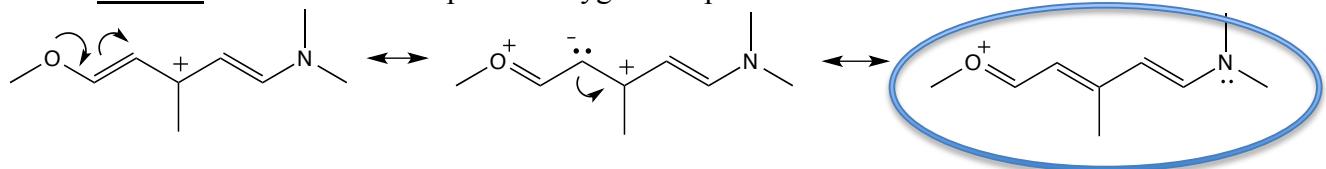


- b) We can resonate into the nitrile groups since the triple bonds are part of our conjugate dpi system. All resonance structures have full octets, but one the original structure minimizes formal charge. Therefore, the starting structure is the most contributing resonance structure.

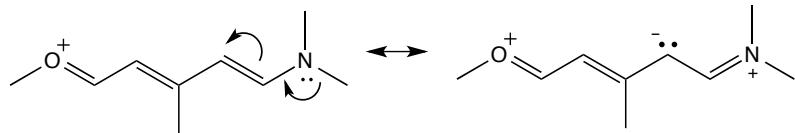


- c) This one's a little tricky. This is easier if you start by moving your lone pairs, rather than starting with the pi bonds. I like to think of resonance structures in terms of paths. Pick one of the lone pairs and pick a direction that you will push them, even if there are multiple options. Begin pushing your electrons down that "path" until it is fully exhausted. Then start with a new set of lone pairs or a new direction and begin the process again.

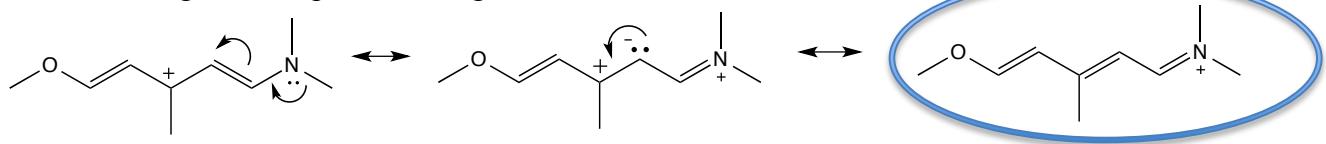
Path 1: Start with the lone pairs on oxygen and push to fill the carbocation.



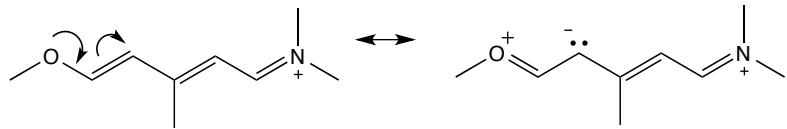
Path 2: Beginning with the last structure from path 1, now push the electron on nitrogen.



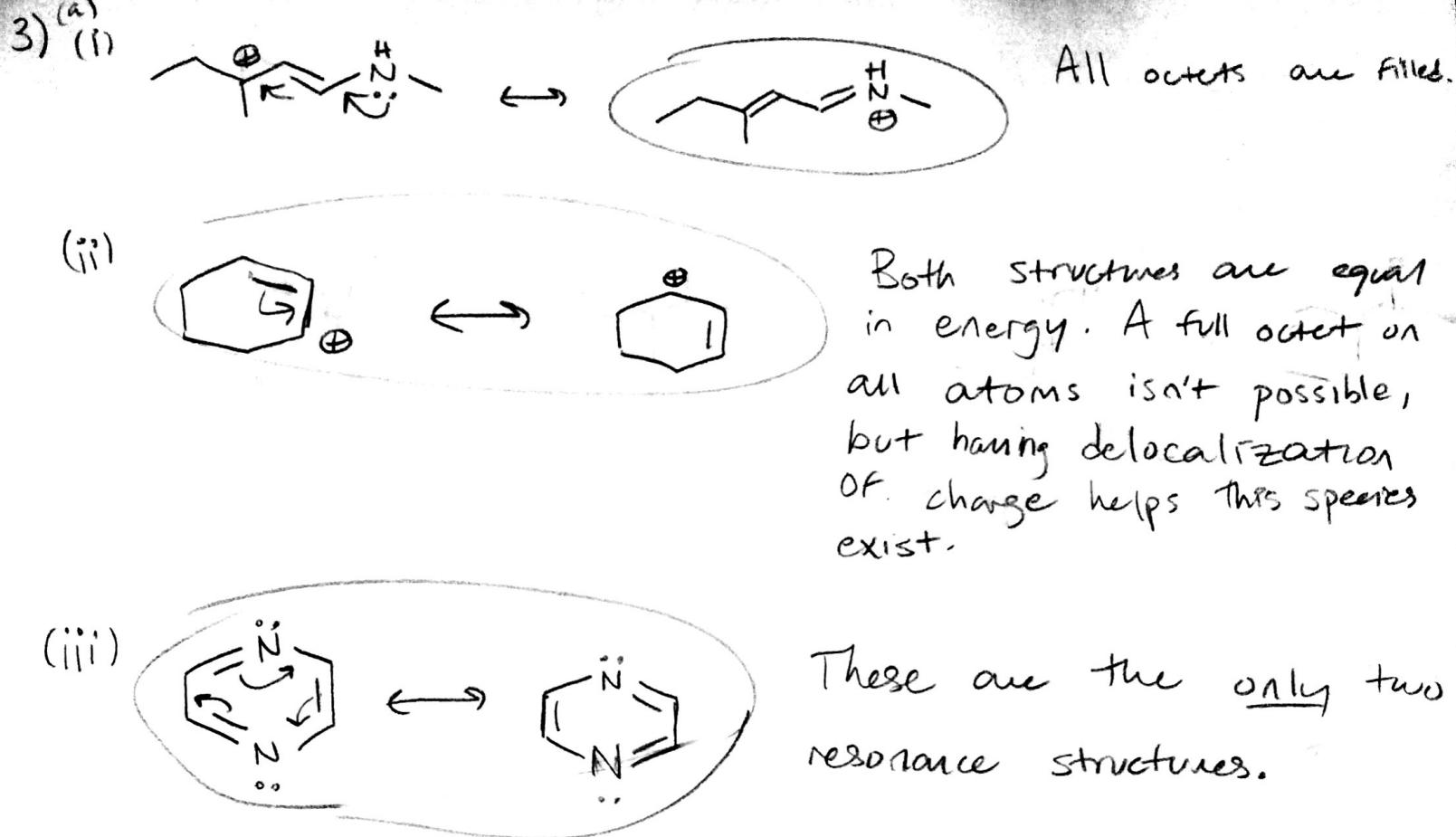
Path 3: Start with the initial structure given in the problem and now start by moving the lone pair on nitrogen first.



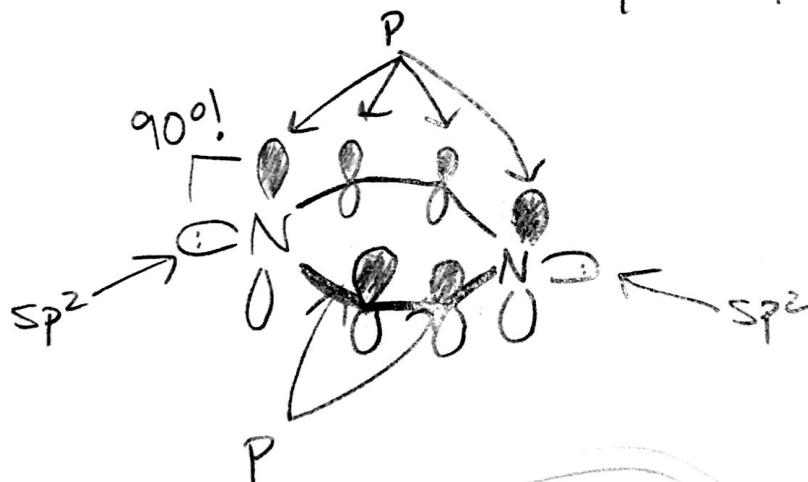
Path 4: Beginning with the last structure form path 3, now push the electrons on the oxygen.



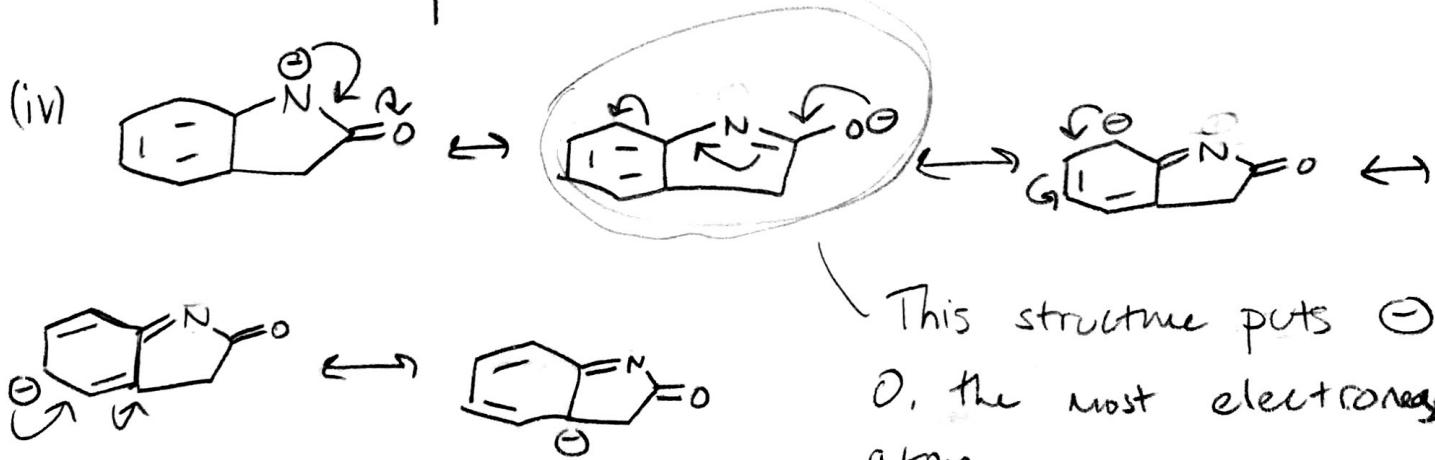
Structures with filled octets and minimized formal charges are most contributing.

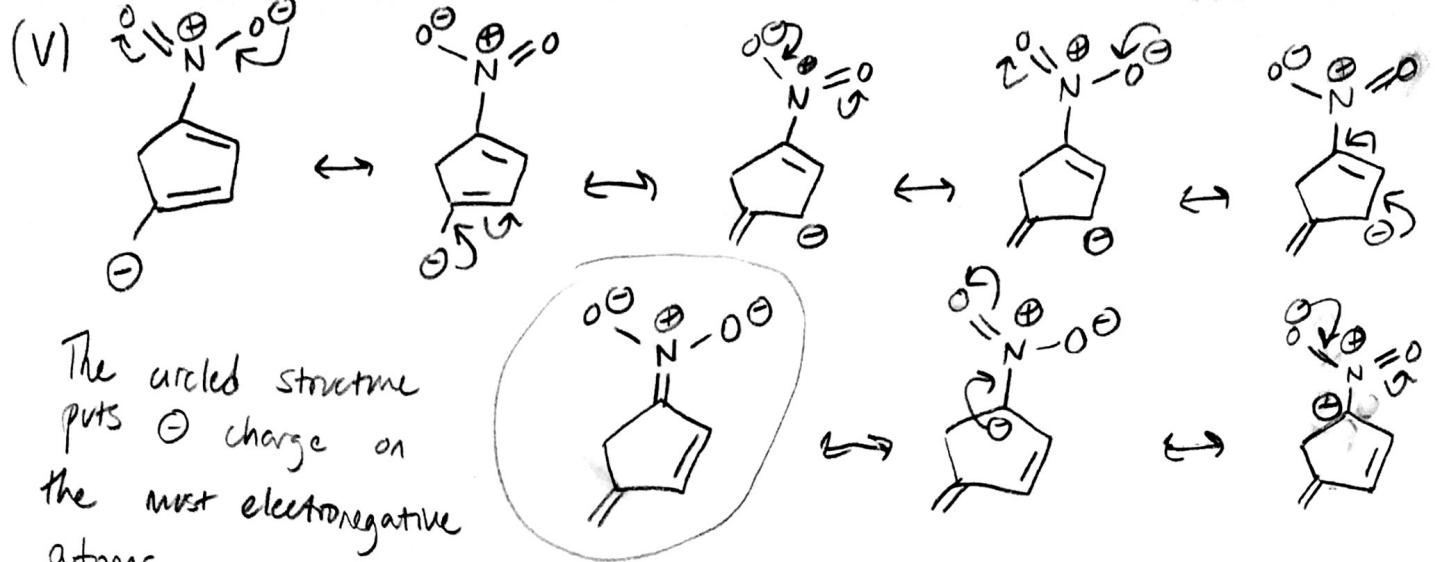


The lone pair on each N are in sp^2 orbitals and are therefore unable to participate in any resonance.

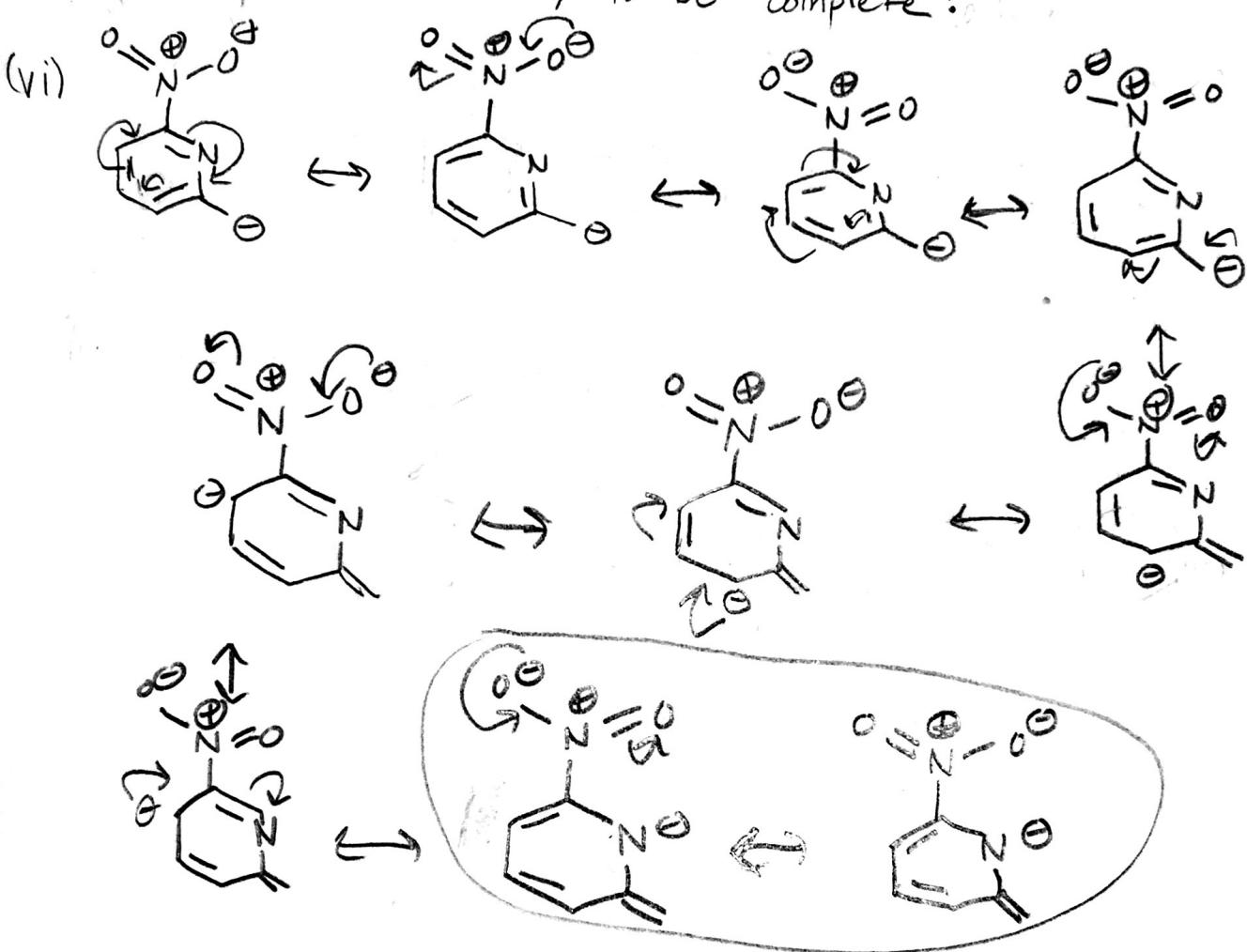


Only e^- in p orbitals can move in resonance structures!



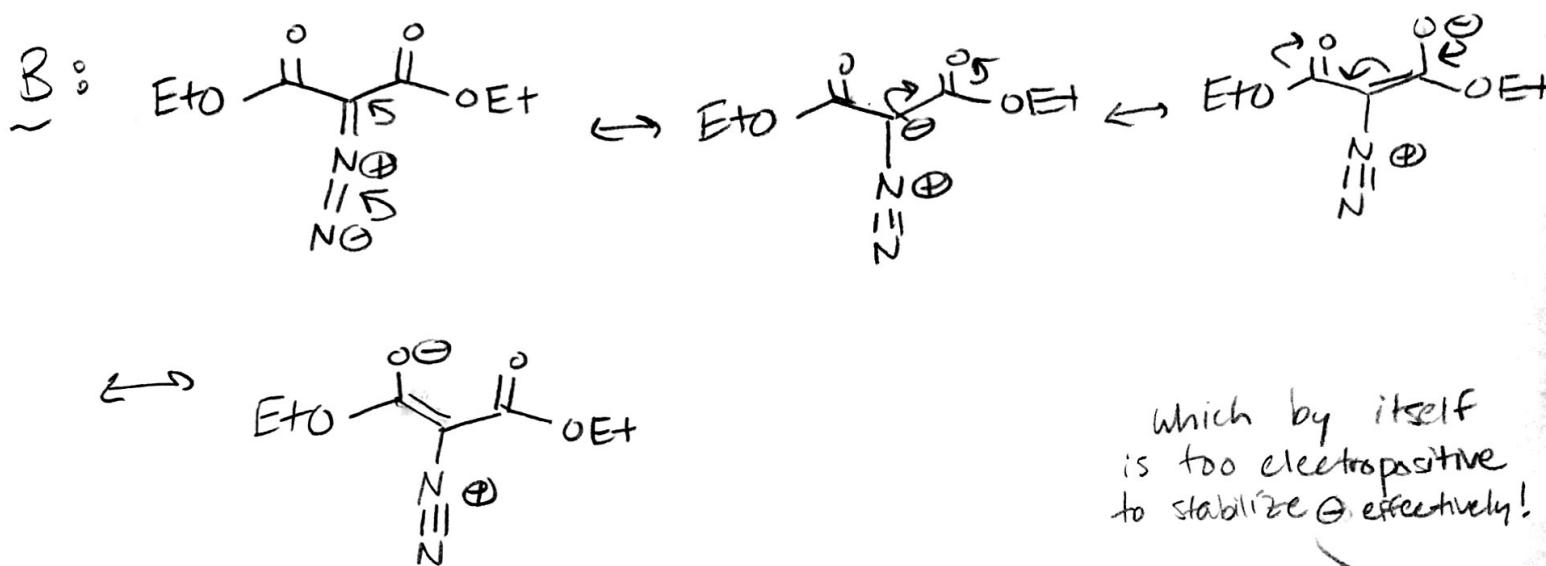
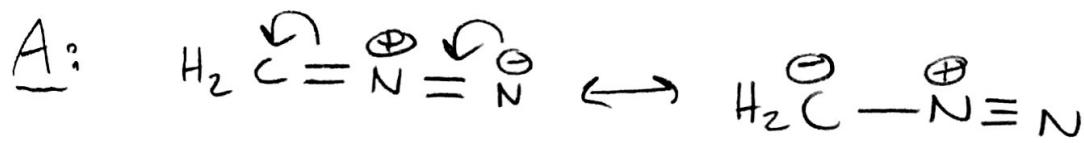


It's a pain in the neck to draw both NO_2 resonance structures every time, but it's necessary to be complete!



The NO_2 only helps stabilize \ominus by induction since it cannot participate in resonance due to its positioning on the ring.

(b) We are concerned with the stability of charge to determine the reactivity of each molecule.



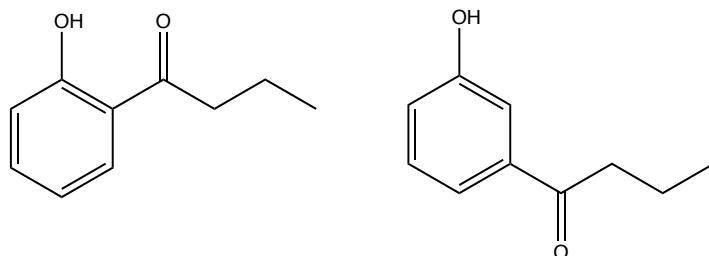
which by itself
is too electropositive
to stabilize \ominus effectively!

As we see above, A has very little stabilization of charge and puts significant \ominus on carbon! B, on the other hand, delocalizes charge across two additional oxygens and is thus very stable.

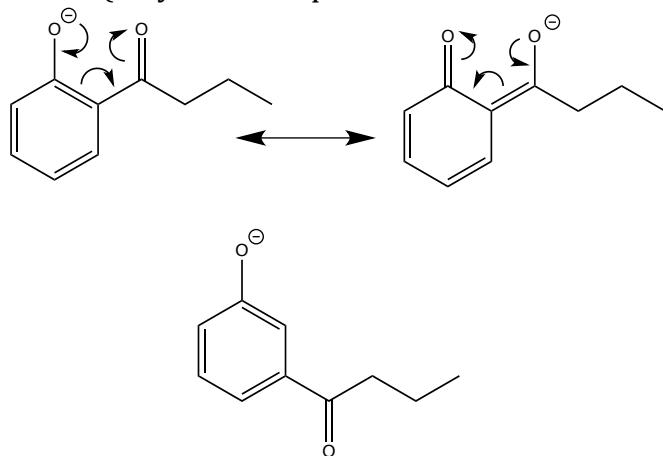
This line of thinking applies broadly to chemical reactivity: When charge in a molecule is unstable, the molecule is reactive!

4) Cross out the weakest acid. Circle the strongest acid.

a)

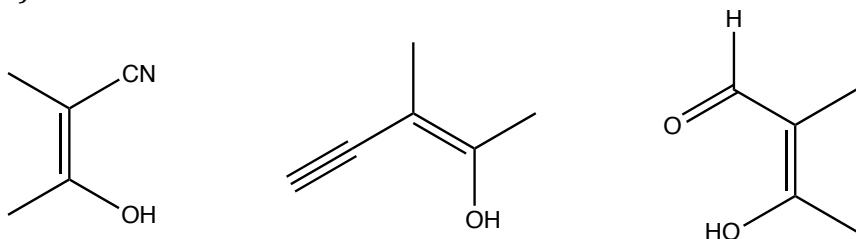


Asking “which of these is the strongest acid” is like asking “which of these has the weakest conjugate base.” We can look at the conjugate bases and their important resonance structures to determine which is the most stable (stable base = weak base). Actually drawing out these resonance structures is very similar to last week’s problem #1- check out the solution there if you’re having trouble! For this problem, I’ve skipped all of the resonance structures that put a negative formal charge on carbon (they’re less important than those with a negative formal charge on oxygen).



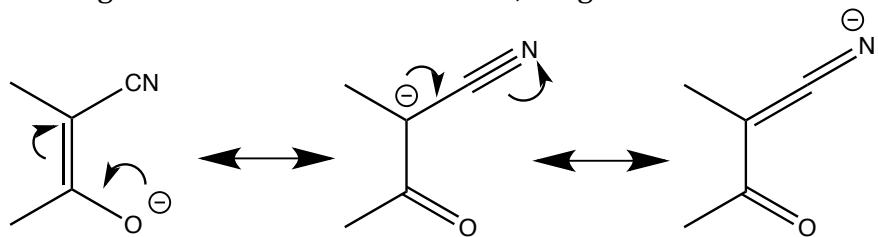
One of these conjugate bases is not like the other- the second conjugate base is less resonance-stabilized than the other, which means that it’s less stable (a stronger base). Stronger conjugate bases indicate weaker acids, so we know that the second acid is probably the weakest. This means the first acid is the strongest.

b)

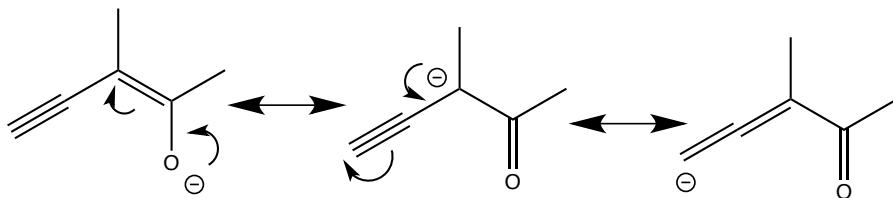


At first glance, it might seem like these are three very different compounds, and we probably cannot guess what the strongest and weakest acids are. However, we can solve this problem the same way that we did the last one- draw out the resonance structures of the conjugate base. This way, we can see which compound has the most stable conjugate base (stable conjugate base = weak base which corresponds to a strong parent acid).

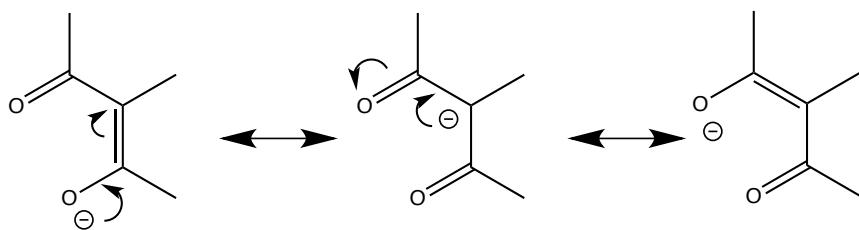
Drawing out our resonance structures, we get:



(Remember that a cyano group, written CN, is just a carbon triple bonded to a nitrogen.)



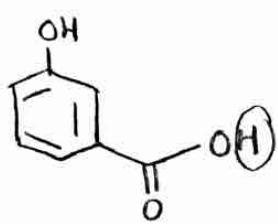
Are you starting to see a pattern emerge? Let's look at the last conjugate base.



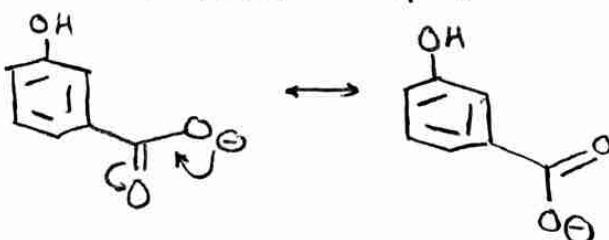
Even though these acids looked different initially, the resonance structures of their conjugate bases show that they have a lot in common. Each has a high-contributing resonance structure on the left (negative formal charge is on oxygen), a low-contributing resonance structure in the center (negative formal charge is on carbon), and a variable resonance structure on the right. The strongest acid has the

weakest conjugate base has the most stable conjugate base has the best resonance structures- this points to the ketone, since its 'variable' resonance structure has the negative formal charge on an oxygen. The weakest acid has the strongest conjugate base has the least stable conjugate base has the worst resonance structures- this points to the alkyne, since its 'variable' resonance structure has the negative formal charge on a carbon.

5(a)



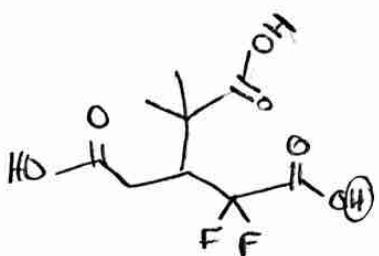
This is the most acidic H because the CB that is formed is more stable than the one that would be formed upon loss of the alcohol H.



The \ominus charge is delocalized between 2 O atoms - which can stabilize the \ominus charge.

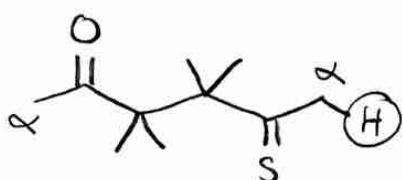
*note: Losing the other H^+ (from the alcohol) would form more resonance structures however they are all less stable since the \ominus charge is delocalized onto C's.

(b)



Due to the inductive effect this H is most acidic - this is because the F's are pulling e- density toward them.

(c)

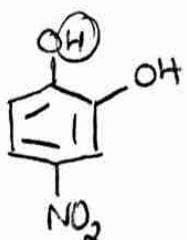


Our possible acidic H's are those α to a C=S and α to C=O. This comes down to a question of conjugate base stability



This is more stable since \ominus charge can be delocalized onto S - a larger atom.

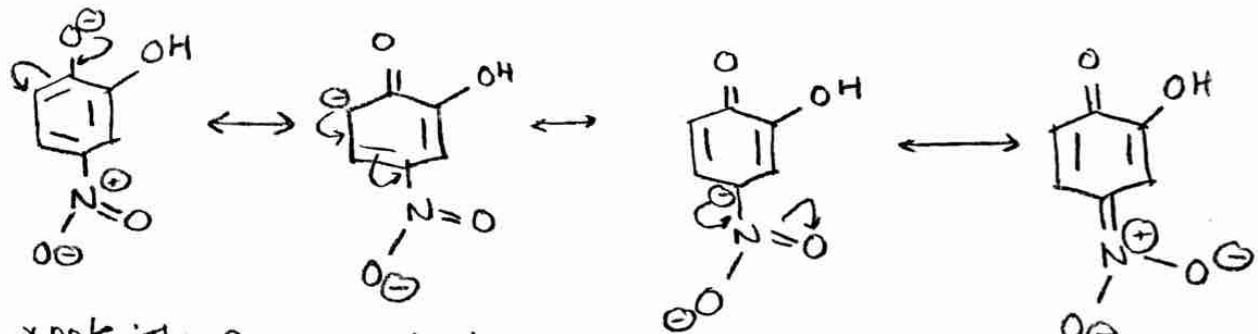
(d)



This H is most acidic as it forms the most stable CB - the e-'s can be delocalized fully onto the NO₂ group. Pulling off the other H would not delocalize the e-'s to the NO₂ group.

*Draw out the resonance structures to prove this *

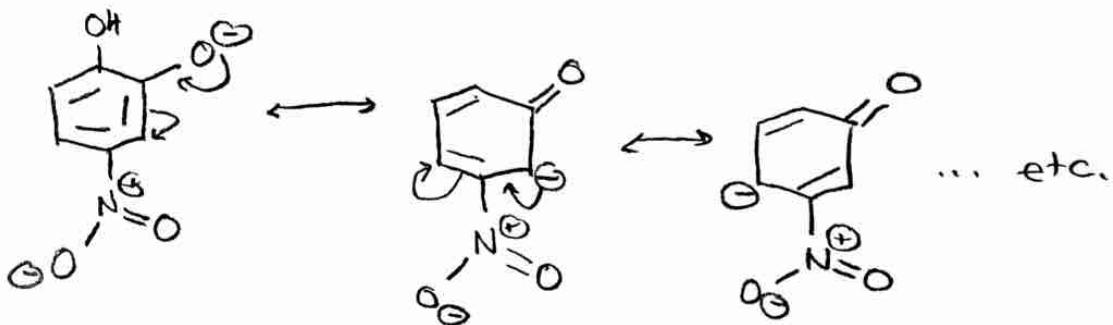
↳ (next page)



*Note: These are not all the resonance structures - I just drew these to show the δ^- charge delocalizing on NO_2 .

$\times \delta^-$ charge is delocalized onto NO_2 !! =stabilized CB,

However if we look at resonance structures OF the CB formed by pulling off the H on the other alcohol, we can't delocalize the negative charge onto the NO_2 .

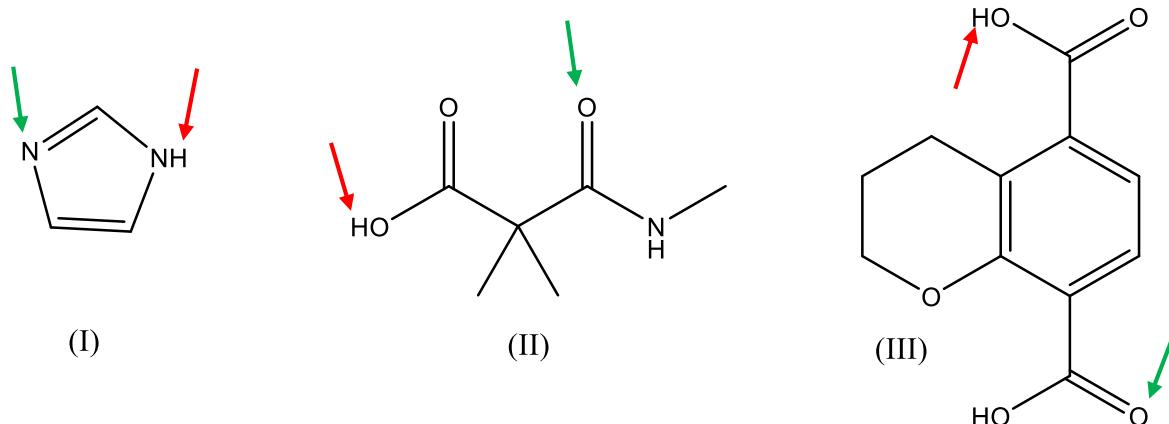


6) For each compound, we'll take acidity and basicity separately. Recall that, in general, you need to be concerned with ***where electrons are*** and ***where they want to be*** when you're thinking about acid-base theory.

To review, you need to be concerned about **charge**, **atomic properties** such as electronegativity and ionic radius, **resonance delocalization** of electrons, **inductive effects**, and **orbital hybridization**, in ***roughly*** that order. The mnemonic I use, then, is **CARDIO** (u need to do more than just get big ok).

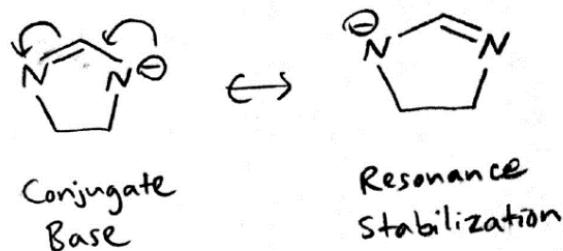
When looking at relative acidity, it is often useful to look at the stability of the conjugate base of each acid. ***Strong acids have relatively weak (or stable) conjugate bases. Strong bases have relatively weak (or stable) conjugate acids.*** This makes logically, too: If an acid is particularly unstable, it will lose its proton fairly easily, and the resulting base will be fairly stable and not very reactive. If it's fairly stable, it doesn't really want to gain a proton, and thus is relatively weak. The same holds true for bases.

So let's take each of these compounds in turn. Red denotes deprotonation site, and green denotes the site of protonation.

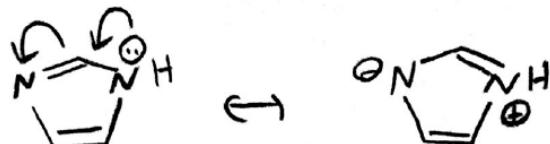


(I) Here we have imidazole, a moiety that appears in the amino acid histidine and is used in affinity chromatography. But you don't care about that, you just want to get an A in organic chemistry. Jerk.

Acidic Site: This one is actually not too bad. Remember that, in general, the hydrogens attached to alkyl groups are not very acidic. The pKa of an alkane is around 50, an alkene is about 43, and a terminal alkyne is about 25. The two common kinds of C-H bonds that are somewhat acidic are the CH bond between a 1,3 diketone ($\text{pKa} \sim 11$) and the alpha-hydrogens of a ketone (~ 20). Both of these are due to resonance. ***However, none of these kinds of C-H bonds show up in this compound.*** Deprotonation of alkene C-H bonds is not very facile, whereas deprotonating hydrogens attached to heteroatoms tends to be easier. Here, deprotonation of the H attached to the nitrogen yields a negative charge which can be delocalized around the ring. This is clearly the most acidic hydrogen.



Basic Site: As mentioned above, there is a resonance structure for this compound which shows negative charge being delocalized onto the left nitrogen, which puts a partial negative charge on the nitrogen. Note that both nitrogens in this compound are sp²-hybridized (they both have a p-orbital in use for pi bonding and resonance), but only the left nitrogen has a partial negative charge on it from resonance.



(II)

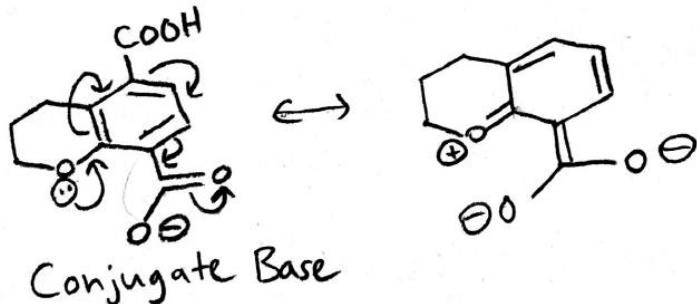
Acidic Site: Hopefully you were able to narrow the acidic site down to either the amide N-H bond or the carboxylic acid O-H bond. Both have a conjugate base which, upon deprotonation, yields an anion which can be delocalized into a carbonyl group, providing anion stability. But recall that oxygen is more electronegative than nitrogen, and thus holds onto negative charge better than nitrogen does. Carboxylic acids are far more acidic than amides ($pK_a \sim 5$ vs $pK_a \sim 16$). For this reason, the hydrogen in the carboxylic acid is the site of deprotonation.

Basic Site: Now, let's apply the logic from above to determine where electrons are sitting in this compound. Because the O holding the H and the N holding the H both have a partial positive charge on them (the resonance structures in which their lone pairs are donated into the carbonyl groups put negative charge into the carbonyl group and a positive charge on the atom holding the H), it is unlikely that those will be the sites of protonation. However, there is partial negative charge on the oxygens of each carbonyl group. So which one has more electron density on it? Recall that nitrogen is less electronegative than oxygen, which means that it can more readily donate electron density into the carbonyl group. There is the greatest amount of partial negative charge on the amide oxygen, and for this reason, it is the site of protonation.

(III) This one is really tough. Let's take it step by step.

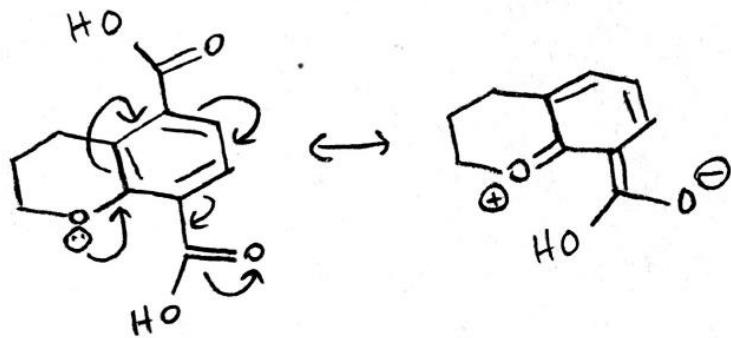
First of all, we note that we have two carboxylic acids present in this compound. There's nothing really to compare in that case. **However, in acid-base problems involving benzene, it is typically the case that the attached substituents will determine the sites of acidity and basicity.** In this case we have a chromane derivative (chromane being this bicyclic compound with benzene attached to a ring with oxygen in it). What is the effect of having an oxygen with lone pairs directly attached to the ring? **We get electron-donation into the benzene ring.**

Acidic Site: Now we have to determine which carboxylic acid is being affected by this electron donation. If we draw resonance structures, we quickly see that the electron density is going into the lower carboxylic acid, but not the upper one. What is the effect of this?



If we examine the deprotonated species which results from each carboxylic acid, we notice that the attached O **competes with the lower carboxylic acid's O(-) to donate electron density into the carbonyl group. The net effect of this is that electron density sits on the lower O(-) more often than it does on the upper carboxylic acid's O(-). This means that the anion which results from the lower carboxylic acid's deprotonation is more unstable than the one which results from the upper carboxylic acid's deprotonation.** It is for this reason that **the upper carboxylic acid is a stronger acid, because its conjugate base is more stabilized.**

Basic Site: We borrow the same logic above to conclude that electron-density is going into the lower carboxylic acid's carbonyl group, as opposed to the upper carboxylic acid's carbonyl group. For this reason, there is a stronger partial negative charge on the lower carbonyl group's carbonyl oxygen, and that is the most basic site on the compound.



7) (a)

$$\text{Degrees of unsaturation} = \frac{(2(\# \text{ carbon}) + 2) - (\# \text{ hydrogen})}{2}$$

$$= \frac{(2(5) + 2) - (8)}{2}$$

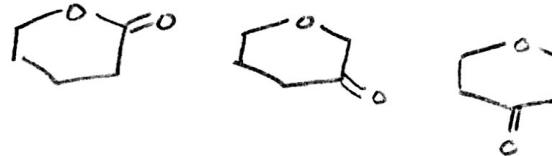
$$= \frac{2}{2}$$

Since we're drawing cyclic isomers with a carbonyl, both degrees of unsaturation are accounted for, so no structure we draw should contain anything but a ring and carbonyl.

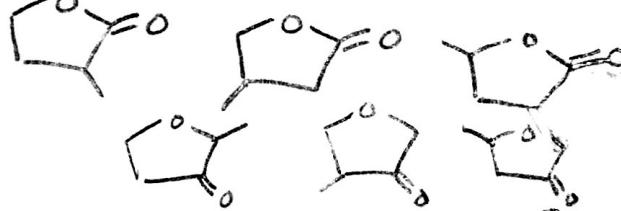
Start with the biggest ring possible and work down.

ring size	isomers
-----------	---------

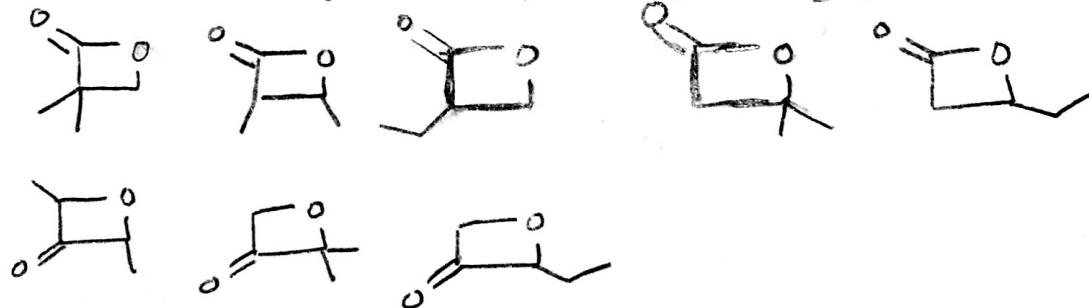
6-Membered



5-Membered



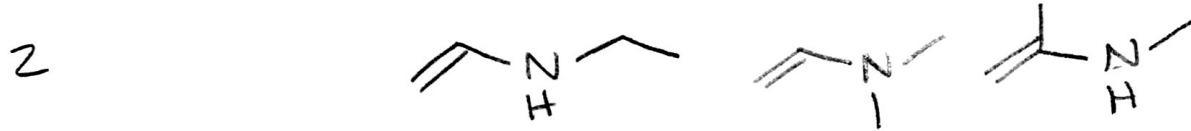
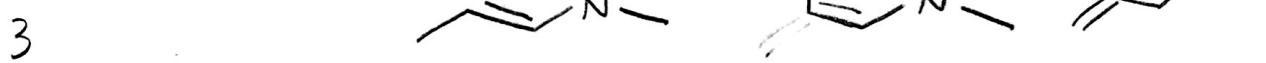
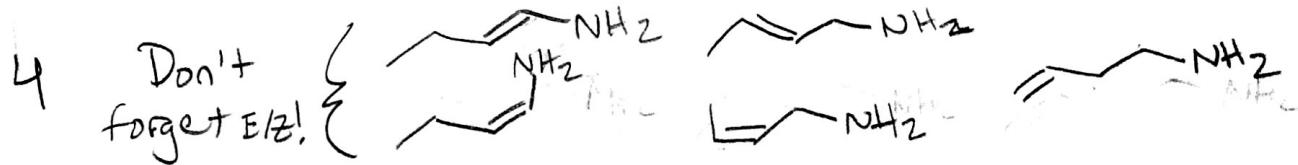
4-Membered



Strategy: in each ring size, position the C=O on the ring and then move any remaining carbons. When all isomers drawn, move C=O and repeat until all unique C=O positions have been shown.

(b) C_4H_9N has 1 degree of unsaturation which will be our $C=C$. Similarly to (a), start with the biggest carbon skeleton possible and work your way through.

longest continuous carbon chain	isomers
---------------------------------	---------



As with all isomer questions, approach them systematically. For (a) & (b), there are many, many isomers, but you should recognize that isomer questions, when broken into parts (e.g. draw all cyclic first, then acyclic), can be mastered.

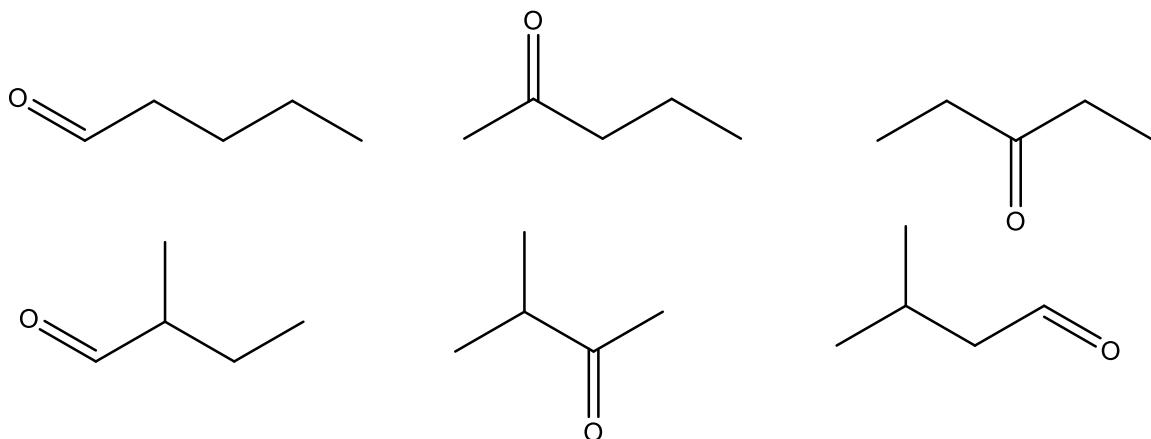
8) First we determine the degree of unsaturation.

$$[(2 \cdot 5) + 2 - 8] / 2 = 2 \text{ degrees of unsaturation.}$$

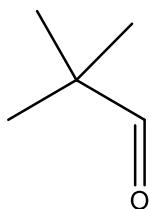
Given that I've specified that you have to use a carbonyl group and that the isomers are acyclic, the other degree of unsaturation MUST come from an alkene.

Our carbon backbones must accommodate a carbonyl group and must also be able to accommodate an alkene being added to it.

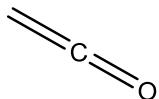
These backbones are as follows:



Note that the following backbone is NOT possible, since there is no place that we can place an alkene without violating the octet rule for the central carbon:



So now we have our backbones. That itself is a bit tricky, but so is this part: You need to place a double bond between C-C bonds and also determine if a stereoisomer can be drawn. In other words, if you draw an E or Z isomer, you need to draw the other isomer as well. Another concern: Getting all of the isomers requires that you also draw **3 ketene molecules**, which is **extremely** difficult to catch. If you didn't get them, don't worry. Note that a ketene looks like this:



If you didn't draw the ketene structures, don't worry about it; it's very, very challenging. Note that a ketene can ONLY be drawn on an unbranching carbon. In other words, it must be drawn from two carbons at the end of a compound, since doing so in the middle of a compound is not physically possible/would violate the octet rule.

Here are all the 19 isomers which result:

Backbone	Isomers

9.

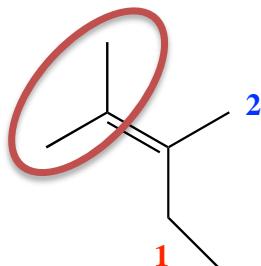
- Label the priority of the substituents off of each double bond
- Indicate whether each bond is E or Z

Each carbon in a double bond has two substituents. To determine if an alkene is E or Z, we must first rank the substituents on each carbon by priority. Each carbon will have one “1” group and one “2” group. If the two “1” groups are on the same side of the double bond, then the alkene is Z. If the “1” groups are on opposite sides of the double bond, then the alkene is E. We can determine the 1/2 priority of substituents with two rules:

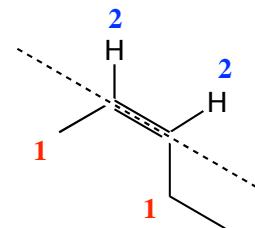
Rule 1: The atom with the higher **atomic number** has higher priority

Rule 2: If rule 1 is a tie, then the atom with the higher **atomic mass** has higher priority

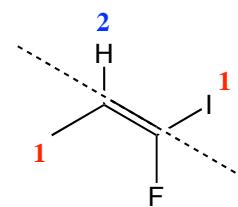
*NOTE: If a double bond carbon has two identical substituents, then the double bond is neither E nor Z:



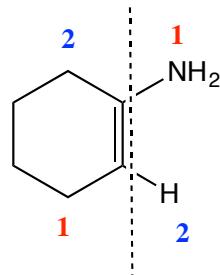
- Hydrogen has a lower atomic number than carbon, so carbon is “1” and hydrogen is “2”. Both “1” groups are on the same side of the double bond (indicated with dashed line) so this is a **Z alkene**.



- Carbon has a higher priority than hydrogen; Iodine has a higher priority than fluorine. “1” groups are opposite side of the double bond, so this is an **E alkene**.

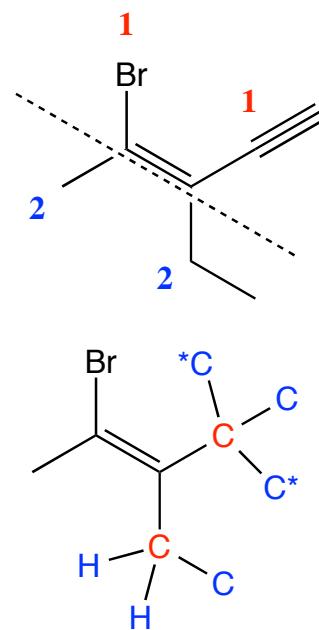


- Nitrogen has higher priority than carbon and carbon has higher priority than hydrogen. “1” groups are opposite side of the double bond, so this is an **E alkene**. **Note:** just because an alkene is in a ring DOES NOT mean it is a Z alkene!



- 4) This one's a little tricky, so let's start with the left side. Bromine has a higher atomic number than carbon, so bromine has a higher priority. On the right side we have a triple bond as one of our substituents. In this case, we want to move out from the double bond one atom at a time. The first atom out from the double bond (in red) for both substituents is the same: carbon. In this case, we have a tie so we continue moving outwards from the double bond. Each of those red carbons is bound to three groups. The bottom one is bound to one carbon and two hydrogens. The top one is engaged in a triple bond with another carbon. We will consider this top carbon as having THREE BONDS TO CARBON (one sigma bond (C) and two pi bonds (C*)). If we line up and compare the substituents for the top and bottom carbons, we get:

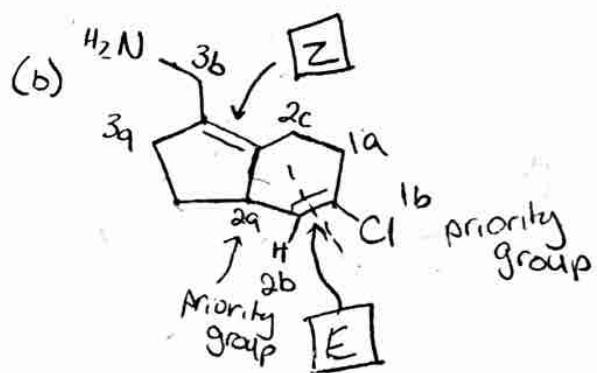
	First	Second
Top Carbon:	C	CC*C*
Bottom Carbon:	C	CHH



Since the bottom carbon has a lower priority hydrogen where the top carbon has a higher priority carbon, **the top group wins and has a higher priority**. Since both "1" groups are on the same side of the alkene, this is a **Z alkene**.



* reminder: you assign priority based on atomic # - that is at the 1st point of difference - the highest atomic #'s get priority.



alkene 1

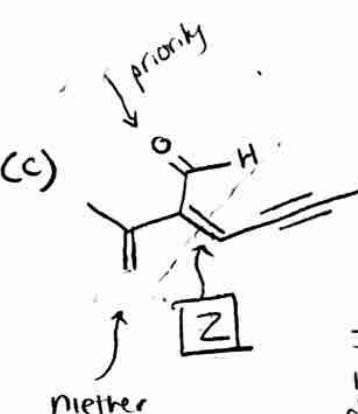
1a (C) vs 1b (Cl)
priority b/c higher atomic #

2a (C) vs 2b H *opposite sides
so E

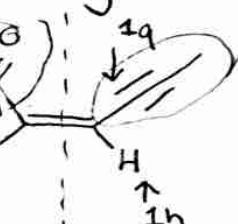
alkene 2

2a (C) vs 2c (C) - same atom so we need to look at what it's bonded to
2a(C) - C, C, H ← this gets priority b/c 2C is

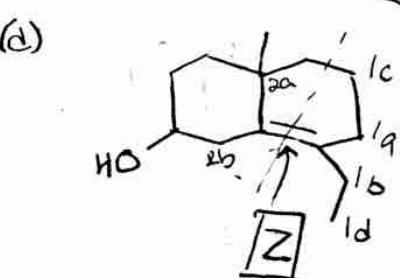
3a vs 3b - 3b gets priority b/c it's bonded to a N. So it's Z



*note:
just redrawn
in a slightly
different
orientation



This alkene doesn't have an E, Z configuration b/c it is achiral!



1) start by drawing a line perpendicular to the double bond. This will be used to separate the two halves + assign priority

2) let's start w/ the right. we're choosing between C(1a) and H(1b) - C has priority

3) Now on the left. At position 1- we have 2 C's - so we have to look at what the C's are connected to.

2a - O, O, H ← we count double bonds as 2 connections
2b - C, C, C

1a has priority!

*Since the groups w/ priority are on the same side, it is Z

1a (C) - C, H, H → need to look 1 down.

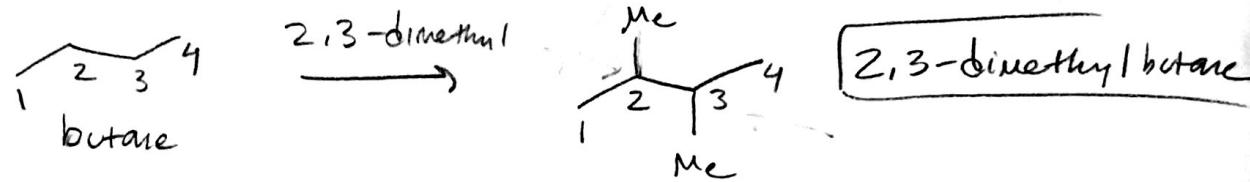
1b (C) - C, H, H → 1c vs 1d.

← side that gets priority

1c (C) - C, H, H
1d (C) - H, H, H

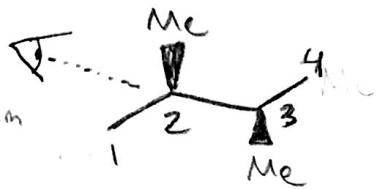
2a (C) - C, H, H
2b (C) - C, C, C ← priority

11. (a) 2,3-dimethylbutane is a butane (C_4 skeleton) with methyl groups on C2 and C3:



(b) We start our analysis with this conformer:

Look down
C2-C3.
for this problem



We rotate C3 60° at a time,
clockwise relative to our viewpoint.

To determine energy of each conformer, I like to make a list of the repulsive interactions present in each conformation. We will start with the conformer shown above and its Newman diagram, then rotate the back carbon 60° at a time until we've completed a full rotation.

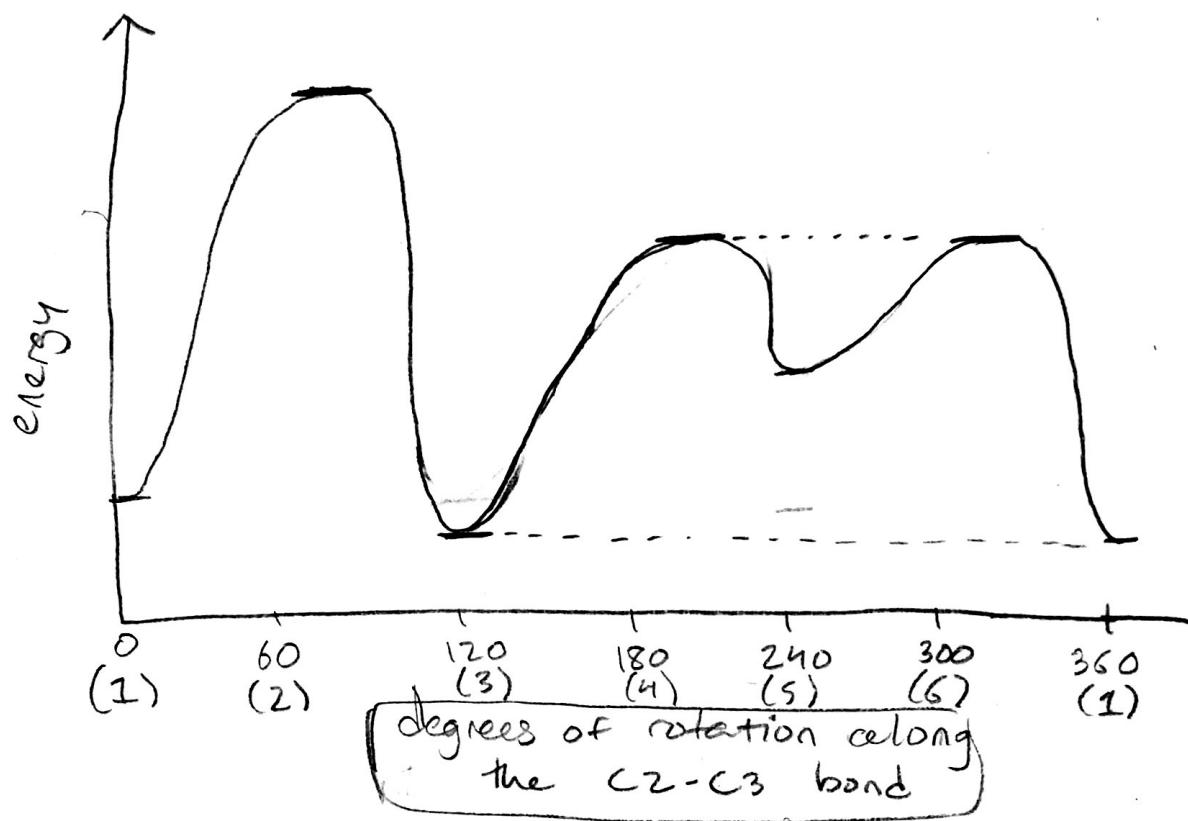
	1	2	3	4	5	6
Newman projection						
repulsive interactions	3x Me-Me 2x Me-H 1x H-H	2x Me-Me 1x H-H	3x Me-Me 2x Me-H 1x H-H	1x Me-Me 2x Me-H	2x Me-Me 4x Me-H	1x Me-Me 2x Me-H

We need only compare 1, 3, and 5, our staggered conformations (minima) and 2, 4, and 6, our eclipsed conformations (maxima).

Comparing 1, 3, 5, we see that 1 and 3 have the same energy, and 5 is lowest in energy due to its minimization of Me-Me interactions.

Comparing 2, 4, 6, we see that 4 and 6 have identical energies, and 2 is higher in energy due to an additional Me-Me (high energy) interaction.

Now, we know the relative energies of our conformers, and can plot energy vs. degrees of rotation:



A few things to note:

- We only need to compare the energies of eclipsed with eclipsed or staggered with staggered
- We can make qualitative energy diagrams that look good!
- Energy is lowest in the staggered conformer that keeps bulky groups far apart, and is highest in the conformer that eclipses the bulky groups

12.

***Important note: I am only asking to which side of the alkene the Br will add. I am **NOT** asking for the product.

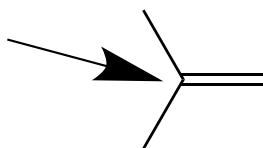
When determining which side of an alkene the Br will add to, it is important to remember that **the stability of the carbocation intermediate** drives this reaction.

The number of non-hydrogen atoms that the carbocation is bonded to determines carbocation stability. The degree of the carbocation is based on the number of carbons that the carbon with the cation is bonded to: a carbocation bonded to only 1 other carbon is a 1° carbocation; a carbocation bonded to 2 carbons is a 2° carbocation; a carbocation bonded to 3 other carbons is a 3° carbocation. You will learn the specific reasons that a carbocation bonded to more carbons is more stable in a few weeks.

In the addition of HBr to an alkene, the Br ends up adding to the **more substituted** side of the alkene because it forms the **more stable carbocation intermediate**.

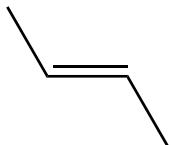
Using this knowledge, let's look at our problems:

a)



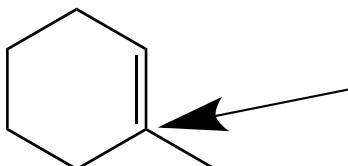
For this alkene, the more stable carbocation will be formed on the left, because it will make a 3° carbocation, as opposed to the right side, which would make a 1° carbocation. Therefore, the Br will add to the left side.

b)



Both sides of the alkene will create a 2° carbocation, so neither side is favored over the other.

c)



For this alkene, the bottom will create a 3° carbocation, while the top will create a 2° carbocation, therefore the Br will add to the bottom.