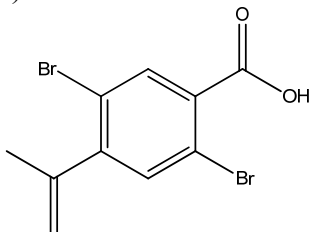


Problem 1 – Name that ~~Tune~~ Molecule

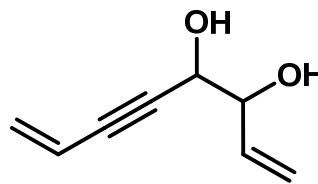
- a) i) 4-ethyl-2,3-dimethylhexane
 ii) 2-isopropylcyclopentanone, OR 2-(1-methylethyl)-cyclopentanone

(2 pts each. Half credit for an incorrect name that would lead to the correct structure. No deductions for extraneous “e” or hyphens)

b) i)

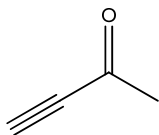


ii)

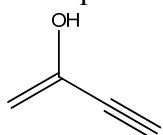


2 pts each. Half credit for one mistake (incorrect bond, one functional group in the wrong position, etc.). No credit if two or more mistakes. May label acid as COOH

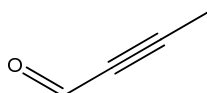
c) Furan has the molecular formula C_4H_4O . You can look up an entire list of valid molecules on NIST Webbook. Here are twelve possible answers. (You only needed to write one of them)



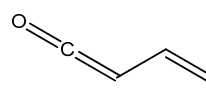
3-butyne-2-one



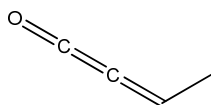
1-buten-3-yn-2-ol



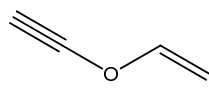
2-butyne-1-ol



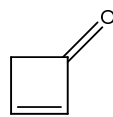
buta-1,3-dien-1-one



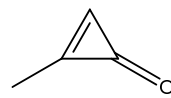
buta-1,2-dien-1-one



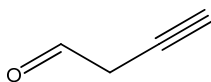
(ethynyloxy)ethene



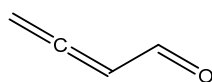
cyclobut-2-en-1-one



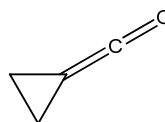
2-methyl-2-cyclopropenone



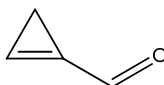
3-butyne-1-ol



buta-2,3-dienal



cyclopropylidenemethanone



cycloprop-1-enecarbaldehyde

2 pts for structure, 2 pts for correct name. Same grading guidelines as above.

d) **BONUS:** 1-cycloheptyl-2,6-diethyl-3,5-dipropylbenzene

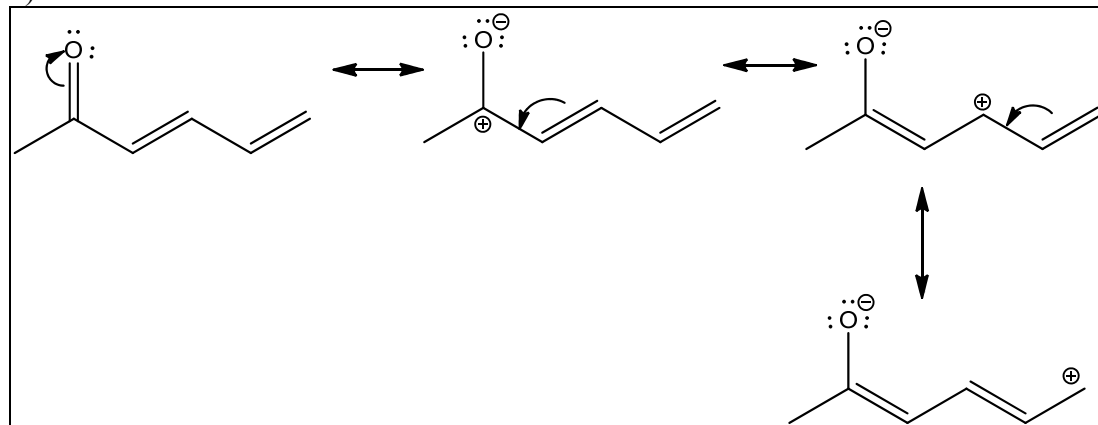
3 pts. -2 for an incorrect name that would lead to the same structure. No credit otherwise

Problem Two – Resonance, Curved Arrow Pushing, and Electro/nucleophiles

a) hexa-3,5-dien-2-one, OR 3,5-hexadien-2-one, OR (3E)-hexa-3,5-dien-2-one

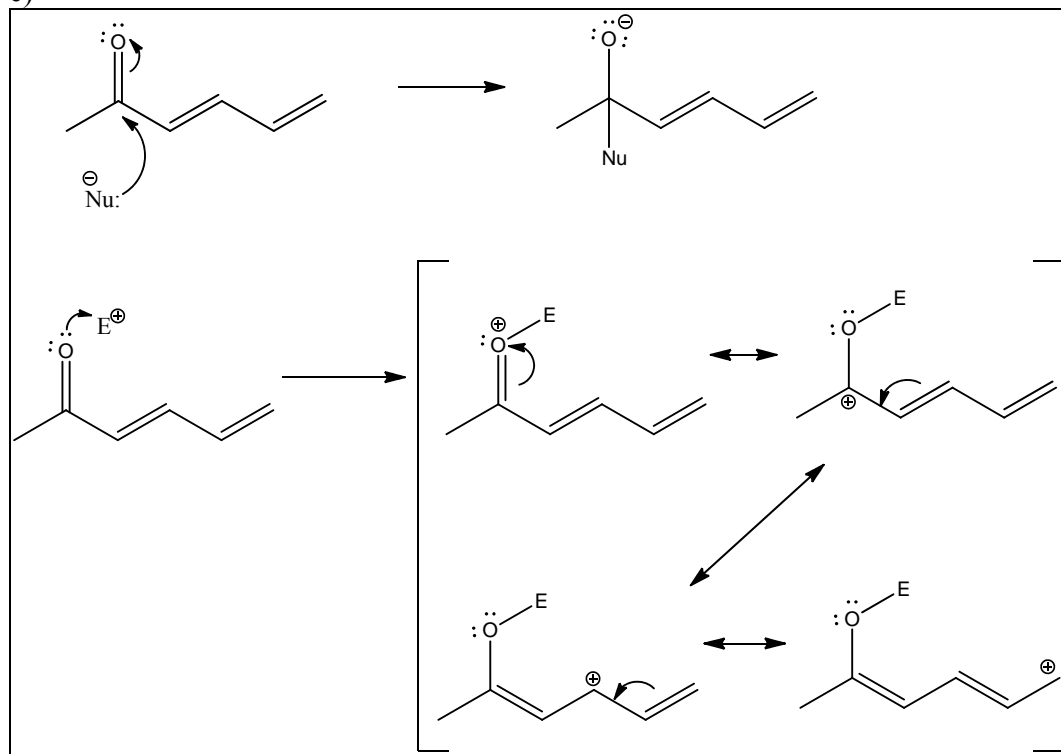
(4 pts. Half credit for an incorrect name that would lead to the correct structure. No deductions for extraneous “e” or hyphens)

b)



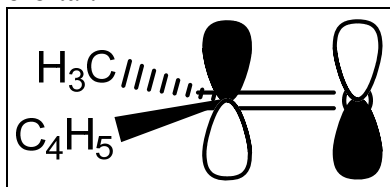
8 pts total. -3 per missing resonance structure, or any structure without lone pairs/formal charges. -2 per incorrect arrow pushing (do not apply in addition to the -3 for missing a structure). Max deduction 8 pts.

c)



2 pts per correct arrow pushing, 2 pts per product that is consistent with the arrow pushing. No credit for any structure missing lone pairs or formal charges. For the second reaction, only ONE of the resonance structures is required for full credit.

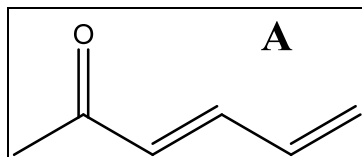
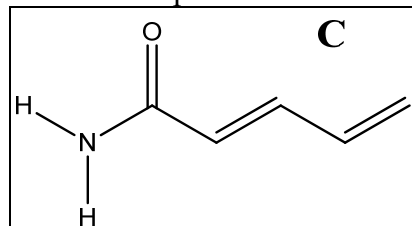
d) A nucleophile donates electrons into the LUMO. For a carbonyl group, the LUMO is the π^* orbital.



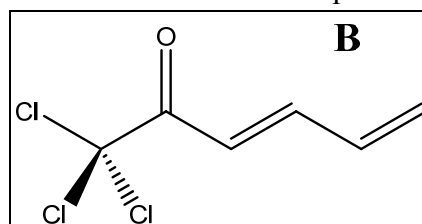
8 pts for the correct orbital. -6 for a drawing that does not clearly show the orbital orientation relative to the rest of the molecule. No credit for an orbital without proper phases. No need to state that the LUMO is involved, or that the orbital is a π^* .

e)

Least electrophilic



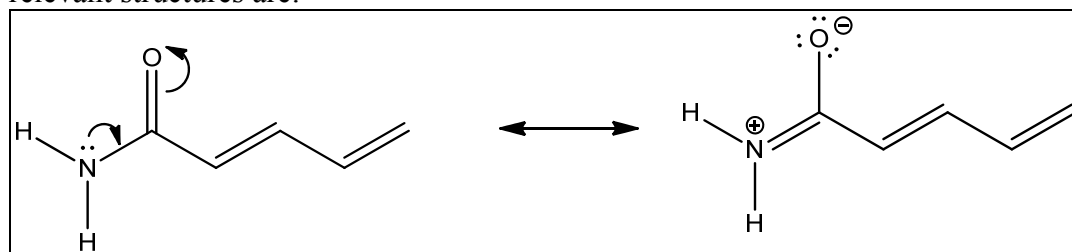
Most electrophilic



Explanation:

B is more electrophilic than A because the chlorine atoms draw electron density away from the carbon, giving it a larger partial positive charge. The negatively charged nucleophile will be more attracted to this more positively charged carbon.

C is less electrophilic than A because the nitrogen atom can push its lone pair electrons onto the carbon of the carbonyl group, giving it extra electron density and resonance stability. The relevant structures are:

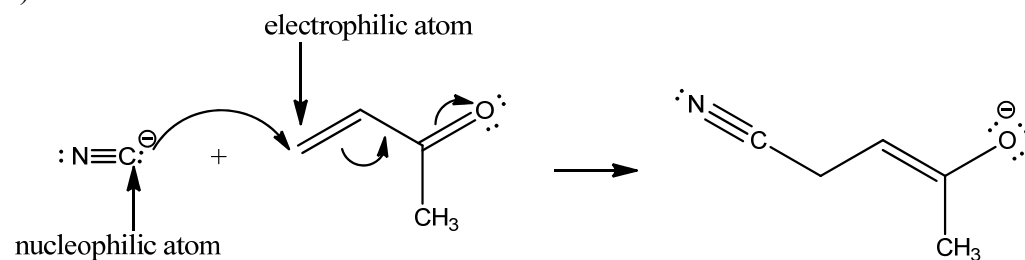


2 pts for correct order, 4 pts per correct explanation. No credit for explanations consistent with an incorrect order. -2 for not drawing resonance structures to explain C, or if structures lack lone pairs/formal charges.

Problem 3 – Eliminate That Boyfriend!

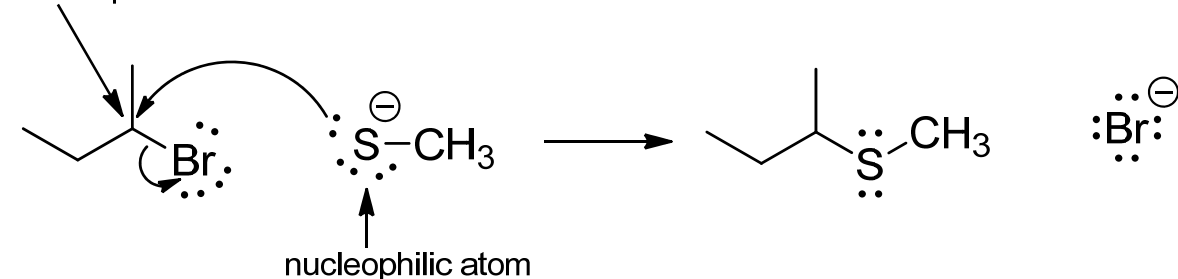
a)

i)



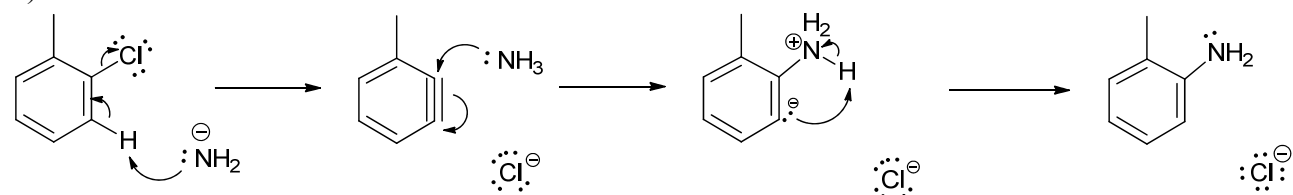
ii)

electrophilic atom



4 pts each (2 pts for labeling nucleophilic and electrophilic atoms, 2 pts for correct product). No credit for incorrect structures or structures missing formal charges or lone pairs. -1 if Br^- is not listed as a product.

b)

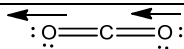
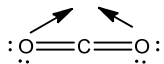
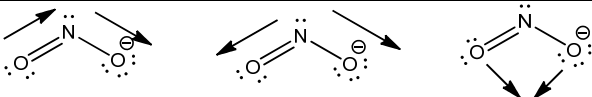
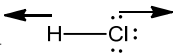


12 pts total (4 pts per part). -3 per part for correct mechanisms that lacks lone pairs. No credit for incorrect arrow pushing.

Problem 4 – Introduction to Spectroscopy

a) Rotational spectrum: must have a permanent dipole.

Vibrational spectrum: any of the vibrational modes must cause a change in dipole.

Molecule	Rot Spectrum?	Vib Spectrum?	IR Active Modes
CO ₂	No	Yes	  and 1 equivalent degenerate mode
NO ₂ ⁻	Yes	Yes	
HCl	Yes	No* (also accept Yes)	N/A  (also accept if answer was Yes)

* Why do you get credit for either answer? The situation is a little complex for HCl. Clearly I chose HCl to teach you a little spectroscopy, and certainly not because I forgot that HCl is not a good molecule for Ch 1.

Your answer depends both on some spectroscopy/quantum mechanics and your definition of “exhibits a vibrational spectrum”. By the rules you’ve learned in class, the vibration changes the dipole, so it should be an active mode. Furthermore, if you couple the vibration to rotation, you’ll see those lines as well, because the dipole still changes.

But here’s the nuance, and you aren’t expected to know this. Closed shell (i.e. all electrons paired) heteronuclear diatomics have two requirements to observe a (pure) vibrational spectrum. First is that the vibration changes the dipole. Second is that the molecule cannot be in a state with no net spin or net angular momentum (we call this a $^1\Sigma^+$ state in spectroscopy). **HCl does not satisfy the second condition, so the pure vibration will be inactive.** But, you will still see lines when the rotation couples to the vibration.

See? Spectroscopy is fun!

10 pts total. -1 per incorrect condition, -1 per incorrect table entry or missing IR mode, including structures missing lone pairs/formal charges. No deduction for not mentioning (or explicitly drawing) the degenerate bend in CO₂, although it will be marked on your paper for informational purposes. Max deduction 10 pts.

b)

$$I = \mu r^2 = \left(\frac{16 \text{ amu} \times 1 \text{ amu}}{16 \text{ amu} + 1 \text{ amu}} \right) \left(\frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right) (0.96966 \times 10^{-10} \text{ m})^2$$

$$I = 1.4695 \times 10^{-47} \text{ kg m}^2$$

(1 pt equation, 1 pt substitution, 2 pts answer. -2 for incorrect sigfigs)

$$\tilde{B} = \frac{h}{8\pi^2 I c} = \frac{(6.62608 \times 10^{-34} \text{ J s})}{8\pi^2 (1.4695 \times 10^{-47} \text{ kg m}^2) (2.99792458 \times 10^{10} \text{ cm s}^{-1})}$$

$$\tilde{B} = 19.050 \text{ cm}^{-1}$$

1 pt equation, 2 pts answer. -2 for incorrect sig figs or units. Award full credit if I was calculated incorrectly in part a, but calculation of the rotational constant is OK.

Spacing in a rotational spectrum is $2B$, so the lines would be separated by 38.100 cm^{-1} .

(2 pts for an answer that is double the rotational constant, even if the rot. constant was incorrect)

c) Spectrum A has a strong absorption in the range $3400\text{--}3200 \text{ cm}^{-1}$, indicating that there is an O–H group. The absorption at 1600 cm^{-1} coupled with the many absorptions in the range $1000\text{--}600 \text{ cm}^{-1}$ indicate a benzene ring. Therefore, Spectrum A belongs to phenol.

Spectrum B also has the strong absorption in $3400\text{--}3200 \text{ cm}^{-1}$ (O–H), but no strong absorption at 1600 cm^{-1} , so it cannot contain a benzene group. Therefore, Spectrum B belongs to 1-butanol.

Spectrum C has both an absorption at 1700 cm^{-1} (C=O stretch) and 2700 cm^{-1} (aldehyde C–H stretch). Therefore, Spectrum C belongs to benzaldehyde.

(2 pts per correct assignment, 2 pts per correct explanation. No credit for an explanation of an incorrect assignment. Accept any alternate logical argument for the assignments except “We already assigned two, so by process of elimination...”)