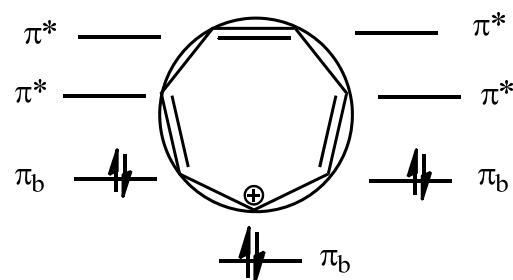


1 – Aromaticity

(1 pt per molecule drawing (1.5 pt for part d), 1 pt. for correct number of π electrons (1.5 pt for part d), 1 pt per Frost circle in parts a–c. 1 pt for each aromatic/antiaromatic. May simply state aromatic/antiaromatic. –1 per circle with unlabeled orbitals. May draw the molecule correctly inside the Frost circle rather than separate molecule/circle)

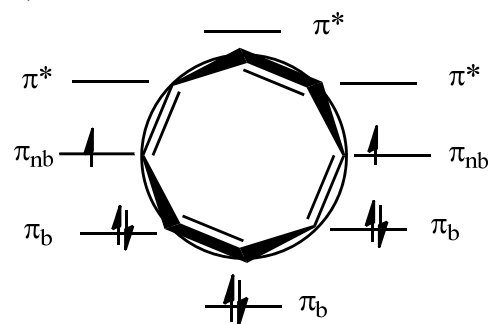
For any of these responses, you could also justify that a molecule is aromatic if the bonding orbitals are completely filled, and the non-bonding/antibonding orbitals are unpopulated.

a)



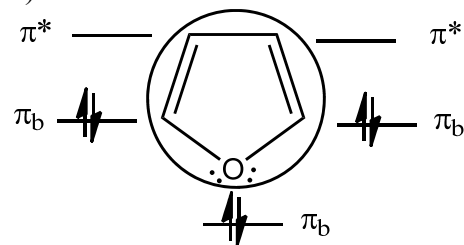
Six electrons satisfy $4n+2$, so aromatic

b)



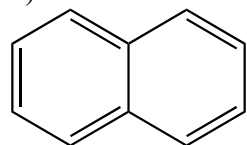
Non-planar, so neither aromatic nor anti-aromatic
OR eight electrons satisfy $4n$, so anti-aromatic
(The first answer is correct, but doesn't comply with our nice simple rule. We'll accept either.)

c)



The oxygen donates one pair of electrons. Six electrons satisfy $4n+2$, so aromatic

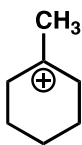
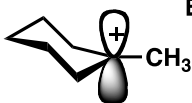
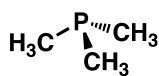
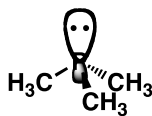
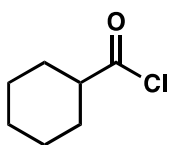
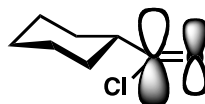
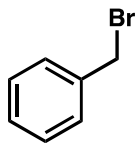
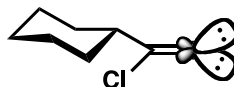
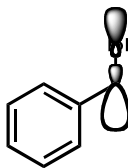
d)



Ten electrons satisfy $4n+2$, so aromatic

2 – Nucleophiles and Electrophiles

2 pt each for correct nucleophile/electrophile/both. 2 pts each for correct orbital drawing (for $\text{C}_6\text{H}_{11}\text{C}(=\text{O})\text{Cl}$, 1 pt. per orbital). No credit for an orbital without correct phases. No deductions if stereochemistry does not match key

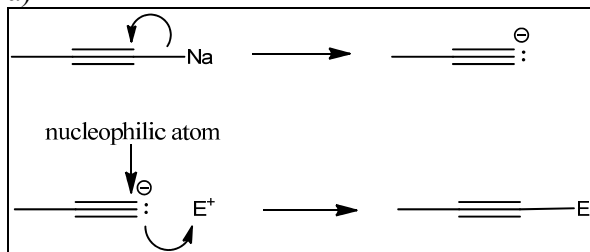
**Electrophile****Empty p orbital****Nucleophile****Filled sp^3 orbital****Carbonyl C: electrophile
O: nucleophile****Electrophile: π^*_{CO}** **Nucleophile: 2 sp^2 n_O
(perpendicular to π^*_{CO})****Electrophile** **$\sigma^*_{\text{C-Br}}$**

3 – Nucleophile-electrophile reactions

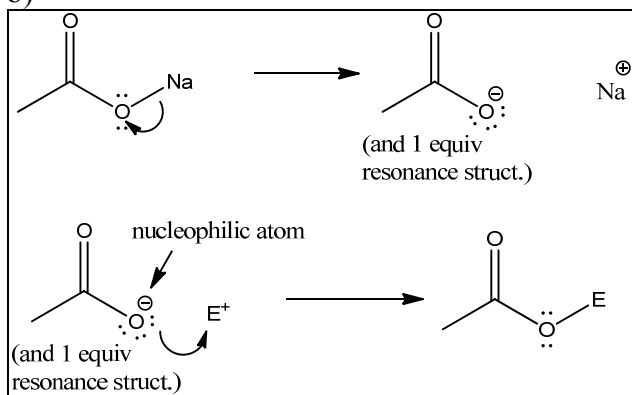
1 pt each for correct identification of nucleophilic atom, 2 pts for correct arrow pushing, 1 pt for correct product. Give full credit for arrow pushing if consistent with wrong nucleophilic atom, etc. No deductions if stereochemistry does not match key. No deductions for not explicitly showing Na dissociation. No deduction for not writing “and x equivalent resonance structures)

Sodium ions will dissociate to form carbanions for (a) and (b). Optional to show this dissociation

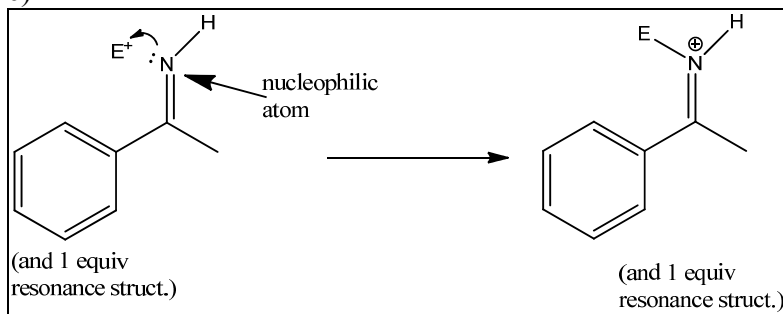
a)



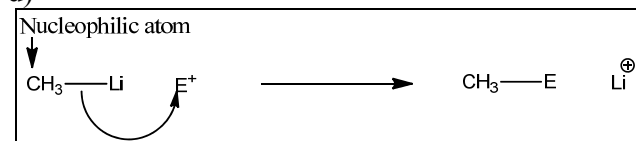
b)



c)

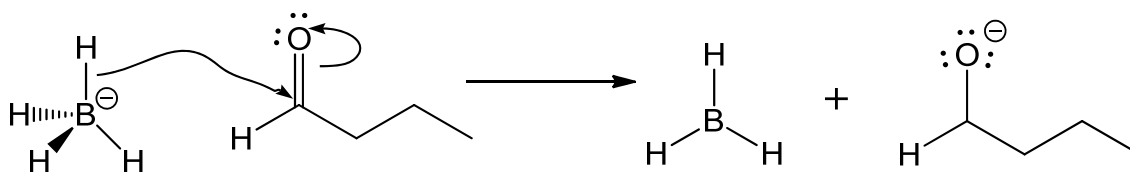
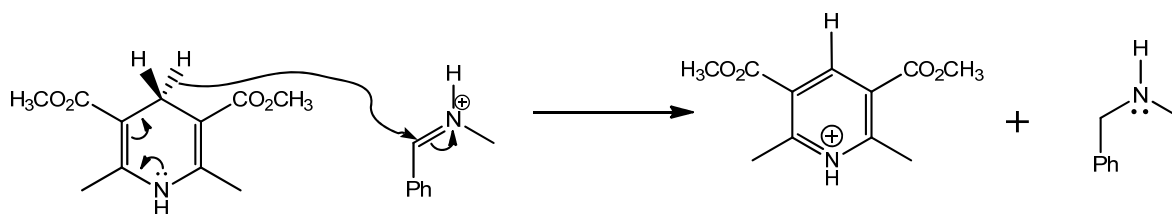
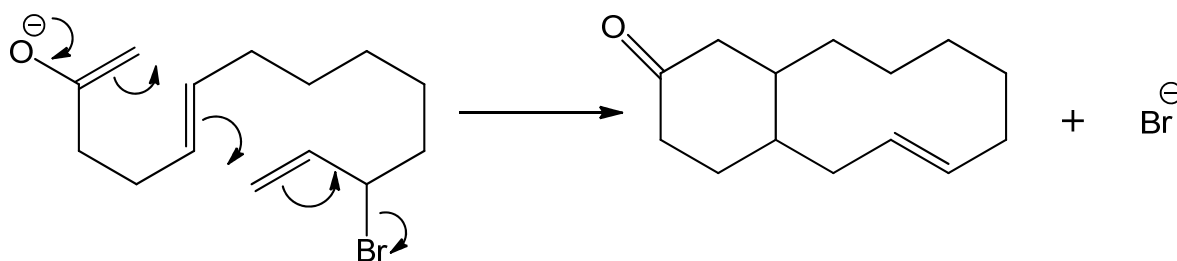
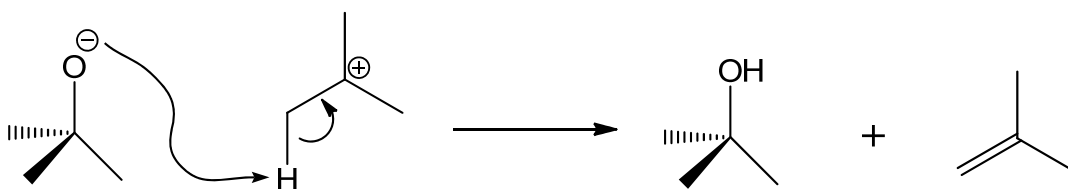
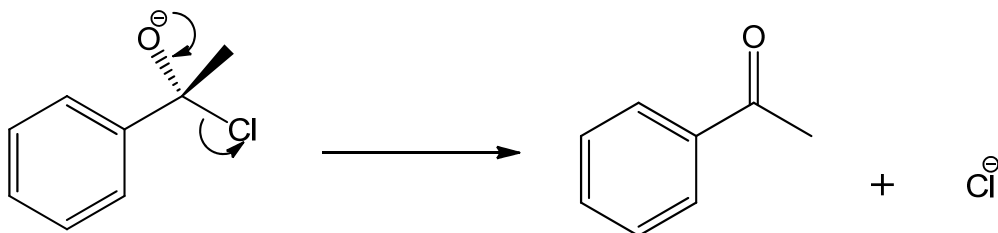


d)



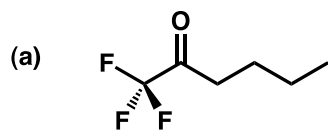
4 – Product prediction

3 pts each. –1 pt for one missing/incorrect product, –3 if both are missing/incorrect. Otherwise no partial credit. No deduction if stereochemistry does not match key. Students may write either 2D structures or 3D structures.



5 – Carbonyl reactivity

2 pt for correct identification of better nucleophile, 2 pts for correct explanation. Structures are not required, but can be drawn and referred to in the explanation.



1,1,1-trifluoro-2-hexanone

The F atoms in 1,1,1-trifluoro-2-hexanone will pull electron density away from the carbonyl carbon by the inductive effect, making it more electrophilic than the carbonyl carbon of 2-hexanone.



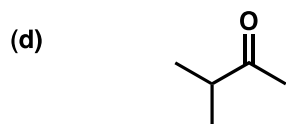
Acetone

The CH₃ groups on acetone are smaller than the C(CH₃)₃ groups on 2,2,4,4-tetramethyl-3-pentanone, so the carbonyl carbon of acetone experiences less steric hindrance.



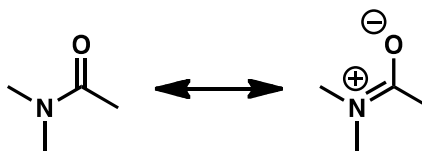
Cyclobutanone

The cyclobutanone ring is strained from its ideal geometry by 30° (120° - 90°). The addition of a nucleophile on the carbonyl carbon will partially relieve this strain (109.5° - 90° = 19.5°). Butanone, on the other hand, is not strained.



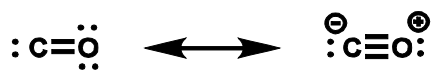
3-methylbutanone

The lone pair on nitrogen of N,N-dimethylacetamide facilitates the formation of a resonance structure that decreases the electrophilicity of the carbonyl, making this molecule less reactive. Specifically, the filled p_N orbital donates electron density into the vacant π*_{CO} of the carbonyl.

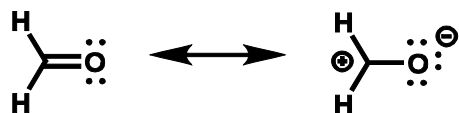


6 – Carbonyl group structural analysis

a) and b)



The triple bond structure is expected to be more prominent in the actual structure because in this structure, both atoms have a full octet of electrons.



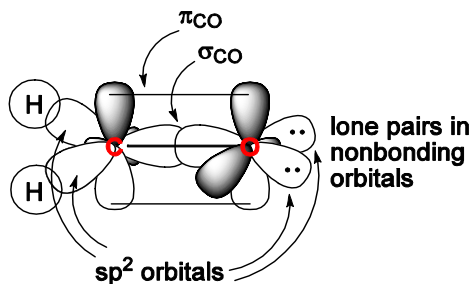
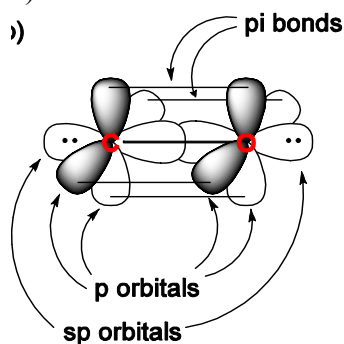
The double bond structure is expected to contribute more to the overall structure because in the zwitterionic structure, carbon does not have a full octet, and there are no functional groups that can help stabilize the positive charge on carbon.

a) 1 pt per resonance structure (total 4 pts) No credit for structures without lone pairs, since we specifically asked you to draw them!

b) 1 pt per comment (total 2 pts).

c)

i)



The hybrid orbital models agree with the more stable of each resonance pair in the Lewis structures from part (a). Specifically, the CO structure contains a triple bond (one sigma bond between sp orbitals plus two pi bonds between p orbitals), while the formaldehyde structure contains only a double bond. It is impossible for a triple bond to exist in formaldehyde, since the C atoms only has one p orbital available for bonding.

4 pts total: 1 pt for each orbital structure, 1 pt each for comparing a molecule to Lewis structures. No credit for any orbital drawing without phases.

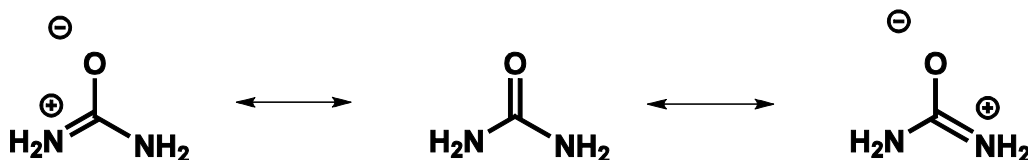
d) The dipole moment of CO is small because in one prominent resonance structure, oxygen, which is more electronegative than carbon, has a positive charge while carbon has a negative charge. In other compounds containing carbonyl groups, the analog of this resonance structure is not present, so charges tend to be localized differently, with carbon carrying a partial positive charge and oxygen carrying a partial negative charge.

You could also mention that since carbon monoxide has a triple bond, its C-O bond length is smaller than formaldehyde or acetone, which reduces μ . However, this only has a small effect, not the large one that you are trying to explain.

(3 points, -1 if only bond length is mentioned. No penalty for ignoring bond length)

e) The presence of the triple bonded resonance structure for CO means that the C-O bond order is greater than 2. Other carbonyl-containing compounds typically have C-O bond orders less than 2, as suggested by the resonance structures. Since triple bonds are stronger than double bonds, it takes more energy to break the C-O bond in carbon monoxide. **(3 points)**

f) Urea should have a stronger dipole moment and weaker CO bond energy than formaldehyde. **(1 point)** The presence of the lone pairs on the nitrogen atoms of urea make three resonance forms possible **(1 point)** which stabilize the zwitterionic structure, meaning that for urea, the CO bond has less double bond character than for formaldehyde. (This is proven by the vibrational frequency observed in IR spectroscopy, where the C-O bond stretch is observed at a lower energy than expected for a typical double bond.) In addition, the oxygen has a stronger negative charge localized on it, and the NH_2CNH_2 portion of the molecule has a stronger positive charge. Since dipole moment strength is dependent on the strength of the charges, urea will have a stronger dipole moment.



1 pt for dipole, 1 pt for weaker CO bond energy, 3 pts for resonance as the reason (do not deduct points for not drawing structures)