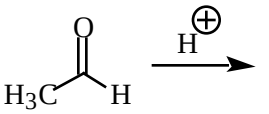
Chemsitry 304B Spring, 1999 Problem Set 6

1. Consider the following data for the major product, **A**, from the following reaction. Note that a minor amount of another isomer is also detected, **B**, which shows the same mass spec and IR properties, but the NMR data are different. [Hint: a carbonl oxygen can be a nucleophile, even if a very weak one]

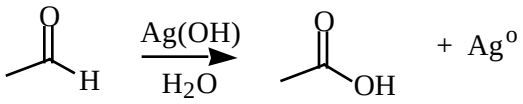


[**A**] IR: no significant peaks in region 1600-4000 cm^{-1} except for C-H stretch
^{1}H NMR: δ 1.1 (3H, doublet, J=7 Hz), 4.8 (1H, quartet, J=7)
^{13}C NMR: two signals 20.0 and 100 ppm
Mass spec: parent ion at 132 mass units (daltons)

[**B**] ^{1}H NMR: d 1.1 (6H, doublet, J=7 Hz), 1.21 (3H, doublet, J=7Hz), 4.8 (2H, quartet, J=7), 4.95 (1H, quartet)
^{13}C NMR: four signals 20.0, 20.5, 98 and 100 ppm

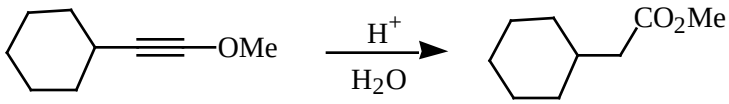
Draw the most likely structures for **A** and **B**, and explain how your structures are consistent with the spectral data. Write a careful mechanism for the formation of **A.**

2. We discussed in class the oxidative metabolism of ethanol to acetic acid with two enzyme-catalyzed steps. The formation of acetaldehyde follows our general mechanism for oxidation of alcohols to aldehydes, but what about the conversion of acetaldehyde to acetic acid?



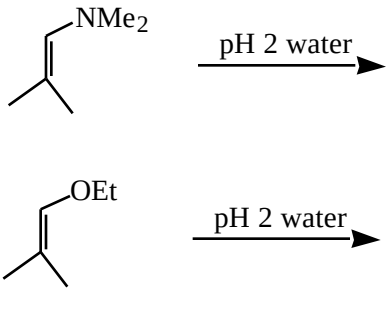
In fact, this conversion is typically slow with conventional oxidizing agents unless water or another weak nucleophile (pyridine) is present in the solution. A standard mixture to carry out this process is silver hydroxide in basic aqueous solution. The products are the acid and silver metal, as a mirror on the flask, which indicates that reaction has occurred. Propose a mechanism which takes into account the presence of hydroxide anion and produces silver metal. [Hint: the oxidation mechanism operates on alcohols. What is the likely reaction between hydroxide anion and the aldehyde?]

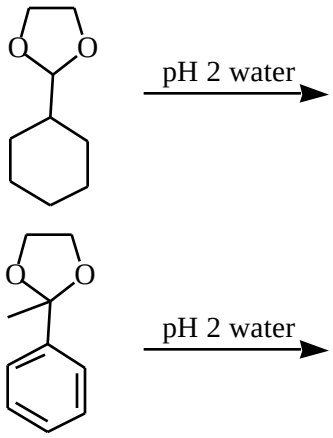
3. Write a stepwise mechanism to rationalize the following conversion:

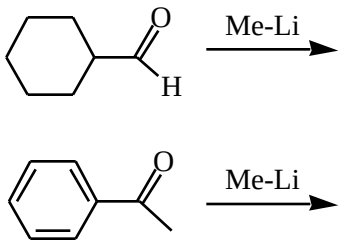


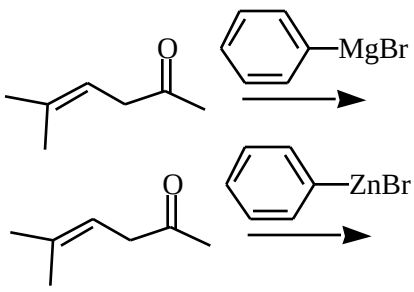
[hint: think of the alkyne as an analog of an alkene]

4. Choose which of the following reactions would be faster and write the product of that reaction. Explain your choice.

A. 

B. 

C. 

D. 

4. Write a stepwise mechanism to rationalize the following conversion.