Disclaimer: This mock exam is only for practice. It was made by tutors in the Polytechnic Tutoring Center and is not representative of the actual exam given by the Academic Department.

Problem 1:

a) Consider the flowing reaction coordinate diagram for an electrophilic aromatic substitution reaction:

b) For the reaction of anisole with bromine and FeBr₃, what are the structures of A, D and G? Draw the structures in the boxes below.

![structures](image)

C) Which of the above compounds are aromatic? Which are nonaromatic? Are any of them antiaromatic? Explain.

Compounds A and G are both 6 π electron aromatic species. None of these compounds are antiaromatic. Compound D is nonaromatic; it has a sp³-hybridized carbon in the ring, blocking full conjugation of the ring.
Problem 2:

a) Choose the correct reagent(s) for each transformation. Write the letter for the reagent choice in the box by the arrow. *None of the reagent choices are used twice.*

b) Which of the above reactions introduce an *electron-withdrawing group (EWG)* onto the arene? **Circle** the EWG on the products.

c) In which of the above reactions is the product arene *more nucleophilic* than the reactant arene? **Label** these products arenes as “more nucleophilic.”

d) For the Friedel-Crafts **alkylation**, which of following RCl would work? Circle all that apply.
**Problem 3:**

a) The following spectra are the regioisomers (meta, para, ortho) of methoxynitrobenzene.

![Spectrum 1: meta-nitroanisole](image1)

![Spectrum 2: para-nitroanisole](image2)

![Spectrum 3: ortho-nitroanisole](image3)

b) Which spectra corresponds to which isomer? Explain your reasoning.

We can quickly determine that Spectrum #2 is the para isomer because there are only 2 peaks in the aryl region, both doublets. This is the pattern for a para-substituted arene where the two substituents are different.

Next we need to distinguish between the ortho and meta isomers. Both compounds have 4 sets of aryl H so we expect 4 peaks in the aryl region (assuming none of the peaks overlap with each other). In both molecules HA will be a doublet and HB will be a triple (or dd, depending on J-values). The easiest ways to tell these apart is to notice that HD in the meta isomer will be a singlet, while NONE of the aryl H in the ortho isomer will be singlets!
Problem 4:

a) Draw in all of the alpha-hydrogens on the structure of pentan-2-one below.

b) Draw all of the possible enolates that can form when pentan-2-one is treated with LDA (a non-nucleophilic, sterically hindered base). LDA does NOT attack the C=O. We use LDA instead of other strong bases (like RLi, RMgBr) to produce enolates for this reason.

c) Are any of these enolates regioisomers? Explain.

Yes, the relationship between A&B or A&C is regioisomeric. The C=C is on a different part of the parent chain.

d) Are any of these enolates stereoisomers? Explain.

Yes, because E/Z isomers are a kind of stereoisomer! Enolates B & C are stereoisomers. Which one of these forms depends on the conformation of the ketone when the reaction happens.

e) The acidity of the alpha-proton on a carbonyl compound depends on the structure of the carbonyl compound.

Which compound is more acidic, ethyl ethanoate or acetone? Explain your answer.

Ethyl ethanoate has a pKa of 24 and acetone has a pKa of 19.3. Lower pKa means more acidic, so acetone is more acidic than ethyl ethanoate. In general, the alpha protons on aldehyde or ketone are more acidic than the alpha protons on an ester or amide. The carbonyl carbon on an aldehyde/ketone is more partially positive than the C=O carbon of an ester or amide. This means than the alpha C-H bond is also more polarized.
Problem 5: The mechanism for oxidation of a 1° alcohol to a carboxylic acid includes an aldehyde and a hydrate of an aldehyde as intermediates. The oxidizing agents that produce carboxylic acids all contain water. This water is needed to form the hydrate of the aldehyde.

a) Which oxidizing agent(s) would you choose to convert butan-1-ol into butanal?

\(CrO_3, H_2SO_4\) \(NaOCl\) \(PCC\) *(gives aldehyde)*

b) Which oxidizing agent(s) would you choose to convert butan-2-ol into butanone?

\(CrO_3, H_2SO_4\) \(NaOCl\) \(PCC\)

c) Which oxidizing agent(s) would you choose to convert butan-1-ol into butanoic acid?

\(CrO_3, H_2SO_4\) *(gives acid)* \(NaOCl\) *(gives acid)* \(PCC\)

d) Even though the aldehyde is in equilibrium with the hydrate, over time all of hydrate is oxidized to carboxylic acid. Explain this with reference to Le Chatelier’s principle.

Le Chatelier’s principle tells us that once an equilibrium has been established, if something perturbs the equilibrium the system then adjusts to get back to the equilibrium state.

In this case, the aldehyde and hydrate are in equilibrium, but the hydrate molecules are further oxidized to carboxylic acid molecules, so it is as if the hydrate (product) is constantly being removed from the reaction mixture. This drives the aldehyde/hydrate equilibrium towards the hydrate, and over time all of the hydrate will be oxidized to the carboxylic acid.