The exam consists of this cover sheet, which contains an extra credit problem, which is optional. There are 10 problems to solve. The time limit for this exam is \textit{1.5 hours} (11:00 am to 12:30 pm). Please read problems carefully so that you understand the entire problem. \textit{No work = no credit.}

\textit{OPTIONAL EXTRA CREDIT (4 points total):}

Show the four possible resonance structures for \textit{p}-nitroaniline in order to receive four points, if you draw them correctly. If you show only three, you will get one point, and no points for less resonance forms.
Chemistry 210
Exam 4 (December 9, 2009)

For problems with reactions, if you need the structure for one of the reactants, you can ask for it, for a 1 point deduction for each reactant requested.

16 1. Show structures for:

- 4-methoxy-2-phenylaniline
- sec-butylbenzene
- p-aminonitrobenzene
- o-bromotoluene
- Benzyl alcohol
- α-xylene
- Anthracene
- Naphthalene

6 2. What is the most interesting aromatic compound you have encountered so far? Give its structure, name and why you like this compound.
6  3. Oxygen is more electronegative than either carbon or bromine. However, phenol is activating for EAS whereas bromobenzene is deactivating. Explain why phenol activates EAS but bromobenzene is deactivating.

Phenol has electron releasing property and B, which has too large of a radius, but when it can donate reg to O.

10  5. The acylium ion can be used as an electrophile for electrophilic aromatic substitution (EAS). (i) Show how you could produce an acylium ion starting starting with the butanoyl chloride shown and AlCl₃ as catalyst (4 pts). (ii) Draw one resonance structure for the resulting acylium ion (3 pts). (iii) Which of these two resonance structures is more stable (3 pts)?

\[
\text{butanoyl chloride} + \text{AlCl}_3 \rightarrow \text{acylium ion}
\]

1(c) #2 is more stable because carbon also has ability of \( \text{Cl}^- \), even \( +1 \) put on "O" atom.
Several electrophiles were discussed that could be used in EAS reactions. Show how you could produce the electrophiles shown below. (Include all reagents that are necessary.) (4 pts eas)

(i) The Br⁻ ion

\[ \text{Br}^- + \text{Br}_3^- + \text{FeBr}_3 \rightarrow \text{Br}_2^- + \text{FeBr}_4^- \]

(ii) The NO₂⁺ (nitronium) ion

\[ \text{HNO}_2^- + \text{H}^+ \rightarrow \text{H}_2\text{O} \]

(iii) The sec-butyl carbocation

\[ \text{C}_4\text{H}_9^+ \rightarrow \text{C}_4\text{H}_9\text{Cl}^- \rightarrow \text{C}_4\text{H}_9\text{C}^- \]

(iv) Using the nitronium ion produced, show how an electrophilic aromatic substitution reaction would occur for addition to toluene. Show the two possible mononitration products (6 pts).

(v) Why would the addition of a second nitronium ion be slower than the first (2 pts)?

Because while \text{CF}_3 is activating when the \text{NO}_2⁺ is added, it will then decrease activity, hence slower reaction.
7. One of the few reactions that destroys the aromatic nature of benzene is the Birch reduction. (i) If you started with toluene, show the correct Birch reduction product (no reaction mechanism is needed). (4 pts).

(ii) Please rank, in order of increasing acid strength (based on $pK_a$ values) of water, ethanol, ammonia and acetylene. (4 pts).

Least acidic: ___________ < ___________ < ___________ < ___________ < Most acidic

12. (i) What is Hückel’s Rule for aromaticity (3 pts)? (ii) Cycloheptatriene is not aromatic, but the cycloheptatriene cation is. Why? (6 pts) (iii) What type of orbital hybridization does each carbon in benzene have? (3 pts)

(c) There needs to be $4\pi^2$ e$^-$ that can move in ring

$n = 0, 1, 2, 3$ e$^-$ = 2, 6, 10 e$^-$

(c) $SP^2$ (trigonal planar bonds; $T_2^*$ bond 90°)
9. Show a single product (no reaction mechanism required), for the monobromination of each of the following compounds (draw the structure of the compound listed first, then attach the bromine group onto the correct carbon).

- Ethylbenzene
- Aniline
- Phenol
- M-xylene
- Benzoic acid
- P-aminobenzoic acid
- Nitrobenzene
- Methyl benzoate (an ester)

10. Please explain why an allylic cation is easier to form than a tertiary cation.

\[ \text{C=C-C}^+ \quad \text{allylic cation} \]

Once formed, can disperse charge through resonance (i.e., move the charge from one carbon to another \( \Rightarrow \hat{\text{C}}-\text{C} \)).

Net effect, spread charge out \( +\frac{1}{2} \text{C}=\text{C}=\text{C}^+ \).