Exam II
2 Nov 2004

Name: ___________________________________________

- This exam contains 4 double-sided pages – **confirm this once you begin**
- Initial every odd page
- The last page is a spectral data table that can be removed
- You will have 80 minutes
- No calculators or models are permitted
- Read all questions carefully – answer the question that is asked!
- Illegible or indecipherable answers may not receive potential partial credit
- Good luck!

1. (4 pts) Provide structures for the following compounds.
   a) *meta*-bromotoluene
   b) 4-chloro-3-methoxybenzoic acid

2. (9 pts) Provide reasonable resonance contributors for the following species. Be sure to include all lone pair electrons and formal charges as appropriate.
   a) \[
   \text{[structure]} \quad \text{[structure]}
   \]
   b) \[
   \text{[structure]} \quad \text{[structure]}
   \]
   c) \[
   \text{[structure]} \quad \text{[structure]}
   \]
3. (18 pts) Provide the structure of the **major** organic product or products expected from each of the following reactions. Write "NR" if no reaction. Indicate stereochemistry where applicable.

- HO\_2\_C\_H\_2\_C\_H\_2 + fuming H\_2\_SO\_4
- \text{Ph} + \text{Br}_2 + \text{FeBr}_3
- Ph + Cl\_2
- (excess) + AlCl\_3 (cat.)
- \text{Ph} - \text{CH}_2\_\text{CH}_2\_\text{Cl} + 1) \text{AlCl}_3 (1 \text{ equiv})
- 2) H\_3\text{O}^+
- HO\_\text{cyclohexane} + BF\_3, 65 °C
- Ph + CH\_2\_\text{Cl}, AlCl\_3 (1 equiv)
- 2) H\_3\text{O}^+
4. (8 pts) One ring of phenyl benzoate undergoes electrophilic aromatic substitution much more readily than the other. 
   
   (a) Circle the more reactive aromatic ring.
   (b) Clearly explain your choice using resonance structures if needed.
   (c) Provide a product you might expect to obtain in good yield if this compound is reacted with a generic electrophile ($E^+$).

![Chemical structure](image)

5. (8 pts) Each of the following reactions contains at least one error. Identify and briefly explain the error(s).

a) 

![Chemical structure](image)

   Error #1:

   Error #2:

b) 

![Chemical structure](image)

   Error #1:

   Error #2:
6. (16 pts) Clearly circle the correct answer for the following questions. There is only one correct answer for each; no credit will be given if more than one answer is circled for each question.

a) UV/Visible spectroscopy is based on _______________ excitation of molecules.
   - nuclear
   - electronic
   - vibrational
   - rotational

b) Which of the following is not an electrophile encountered in electrophilic aromatic substitution (i.e., which will not work as $E^+$)?
   - acylium
   - carbocation
   - bromine
   - nitronium

c) Which of the following is not aromatic?

[Images of different structures]

d) Which of the following is not aromatic?

[Images of different structures]

e) Which of the following will exhibit the longest $\lambda_{\text{max}}$?

[Images of different structures]

f) Electrophilic aromatic iodination can be accomplished with?

- conc HI
- $I_2$, $AII_3$
- $I_2$, HNO$_3$

[Images of different structures]

g) Preparation of alkyl benzenes is best accomplished via Friedel-Crafts acylation followed by treatment with ____________.

- Zn(Hg), aq HCl
- PCC
- SOCl$_2$

h) Each additional alkyl substituent attached to a conjugated pi system increases $\lambda_{\text{max}}$ by about ____ nm.

- 1 – 2
- 4 – 5
- 30 – 40
- 90 – 100

i) Which of the following will react fastest towards an electrophile ($E^+$) in an EAS reaction?

[Images of different structures]
7. (8 pts) Provide a complete and detailed mechanism for the following reaction. Be sure to clearly show arrows, lone pairs, and formal charges. Messy or indecipherable work will not receive potential partial credit.

\[
\begin{array}{c}
\text{H}_2\text{SO}_4 \\
\text{HNO}_3
\end{array}
\rightarrow
\begin{array}{c}
\text{H}_2\text{SO}_4 \\
\text{HNO}_3
\end{array}
\]

8. (4 pts) Provide a mechanism that accounts for the formation of the highly electrophilic acylium ion from propionyl chloride and AlCl₃. Be sure to clearly show arrows, lone pairs, and formal charges and draw the resulting acylium ion intermediate in the box.

\[
\begin{array}{c}
\text{O} \\
\text{Cl}
\end{array}
\rightarrow
\begin{array}{c}
\text{O} \\
\text{Cl}
\end{array}
\]

9. (4 pts) Cyclobutadiene (shown at right) is planar and contains a cyclocontinuous arrangement of \( p \) orbitals. It is anti-aromatic. Explain why this is the case using Frost’s circle (aka polygon rule).
10. (10 pts) The $\Pi_2$ molecular orbital (MO) for the allyl system is shown below.
   a. Complete the allyl MO system by drawing correctly phased p-orbitals for $\Pi_1$ and $\Pi_3$ on the lines provided on the left.
   b. Place the appropriate number of electrons in the allyl cation, anion, and radical systems.
   c. For the allyl cation, the LUMO is (circle one): $\pi_1$ $\pi_2$ $\pi_3$
   d. For the allyl anion, the HOMO is (circle one): $\pi_1$ $\pi_2$ $\pi_3$

11. (11 pts) Complete the boxes for the following ‘roadmap’ problem. Spectra are listed on the following pages.

$^{13}$C NMR data for Compound A: 122, 127, 130, 131 ppm

A contains Br

B \[ \text{NaBH}_4, \text{CH}_3\text{OH} \]

C
$^1$H, $^{13}$C NMR, and IR for Compound B:

![Chemical Spectra](image)
IR for Compound C:

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