Chemistry 52  
Exam #1

Name: ____________________________ 22 January 2003

This exam has six (6) questions, two cover pages, six pages, and 2 scratch pages.

Please check before beginning to make sure no questions are missing.

65 minutes have been allotted for completion of the exam.

All scratch work should be done on the attached blank pages, which will be collected.

Please sign BOTH cover pages.

Make sure that your final answers are clearly indicated and that you clearly cross out any mistakes!!
Name: __________________________

1. _____ (10)

2. _____ (8)

3. _____ (25)

4. _____ (15)

5. _____ (21)

6. _____ (11)    TOTAL: _____ (90)

TIPS:

- Look over the entire exam first so you can better divide up your time.

- If you get stuck someplace, try drawing out the structures and thinking about where electrons might move to.

- If you really get stuck on a problem, move on and come back to it later.
1. **Multiple choice questions.** Circle the *best* answer for each question. (2 pts. each)

A. In which answer are the alcohols arranged from most acidic to least acidic?
   a) *p*-nitrophenol, phenol, *tert*-butanol, methanol
   b) phenol, *p*-nitrophenol, methanol, *tert*-butanol
   c) methanol, *tert*-butanol, *p*-nitrophenol, phenol
   d) *p*-nitrophenol, phenol, methanol, *tert*-butanol
   e) phenol, *p*-nitrophenol, *tert*-butanol, methanol

B. As substituents in electrophilic aromatic substitution, halogens are:
   a) deactivating ortho-/para-directors because they are much larger atoms than carbon
   b) deactivating ortho-/para-directors because of electronegativity and due to poor orbital overlap between the halo-group and the cationic intermediate
   c) deactivating meta-directors because of electronegativity
   d) activating ortho-/para-directors because halogen *p*-electrons can be donated to stabilize the cationic intermediate.
   e) activating meta-directors because of steric bulk.

C. Friedel-Crafts alkylation of 1,3-dimethylbenzene with *tert*-butyl chloride occurs primarily at carbon 5 because:
   a) one ortho-/para-director cancels the other out and meta-substitution becomes favored
   b) the alkylation does not actually proceed by an electrophilic aromatic substitution mechanism.
   c) the normally more rapid substitution at the other positions is slowed by steric hindrance
   d) the para-substituted product rearranges to the less sterically hindered product
   e) the laws of nature are suspended for this type of reaction.

D. Which of the following sequences of reactions would convert toluene to 4-bromo-3-nitrobenzoic acid (*note: here ‘bromination’ refers to treatment with FeBr₃/Br₂*)
   a) nitrination, bromination, KMnO₄ oxidation
   b) KMnO₄ oxidation, bromination, nitrination
   c) bromination, nitration, KMnO₄ oxidation
   d) nitrination, KMnO₄ oxidation, bromination
   e) bromination, KMnO₄ oxidation, nitrination
E. The conversion of an alcohol into an alkyl chloride by reaction with thionyl chloride is best described as an example of:
   a) an electrophilic addition process
   b) an E2 process
   c) an SN2 process
   d) an E1 process
   e) an SN1 process

2. Treatment of 2-nitrophenol (1) with sodium hydroxide yields sodium 2-nitrophenoxide. Using arrows to indicate movement of electrons:
   (1) draw a mechanism for the deprotonation reaction and
   (2) draw all resonance structures for the stabilized phenoxide (don’t forget the obvious one). (8 pts.)

   ![Structure of 2-nitrophenol](image)
3. Predict the major product for each set of reactions given below. Show intermediate products in the spaces provided. You must draw your final product in the box to receive credit. (5 pts. ea., 25 pts. total)

a) \[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{C} \quad \text{C} \\
\text{H} \quad \text{Cl} \\
\end{array}
\xrightarrow{\text{H}_3\text{C}}
\begin{array}{c}
\text{H}_3\text{C} \\
\text{AlCl}_3
\end{array}
\xrightarrow{\text{excess KMN0}_4}
\]

b) \[
\begin{array}{c}
\text{OH} \\
\end{array}
\xrightarrow{\text{CrO}_3, \text{H}_3\text{O}^+, \text{acetone}}
\begin{array}{c}
\text{pyridine:} \\
\end{array}
\xrightarrow{\text{POCl}_3}
\begin{array}{c}
\text{1H NMR: No resonances} \\
\text{from 4.5 - 6.5 } \delta
\end{array}
\]

c) \[
\begin{array}{c}
\text{br2/FeBr}_3 \\
\end{array}
\xrightarrow{\text{excess KMnO}_4}
\begin{array}{c}
\text{H}_3\text{C} \\
\text{AlCl}_3
\end{array}
\xrightarrow{\text{excess KMN0}_4}
\begin{array}{c}
\text{H}_3\text{C} \\
\end{array}
\]

d) \[
\begin{array}{c}
\text{Cl} \\
\end{array}
\xrightarrow{\text{excess KMN0}_4}
\begin{array}{c}
\text{H}_3\text{C} \\
\text{AlCl}_3
\end{array}
\xrightarrow{\text{excess KMN0}_4}
\begin{array}{c}
\text{H}_3\text{C} \\
\end{array}
\]

e) \[
\begin{array}{c}
\text{1)} \text{BH}_3 \\
\text{2) NaOH/H}_2\text{O}_2 \\
\text{3) PCC}
\end{array}
\xrightarrow{\text{IR: No band from 3300-3400 cm}^{-1}}
\begin{array}{c}
\text{1)} \text{PhMgBr} \\
\text{2) H}_3\text{O}^+ \\
\text{3) CrO}_3, \text{H}_3\text{O}^+ \\
\text{acetone}
\end{array}
\]


\[ \text{A} \]

i) Would you expect the aromatic ring in compound A to be (choose one): (5 pts)

- a) deactivated by induction and resonance  
- b) deactivated by induction but activated by resonance  
- c) activated by induction but deactivated by resonance  
- d) activated by induction and resonance  
- e) not activated at all.

ANSWER: 

ii) Explain your prediction and indicate which *aromatic* carbons would undergo the fastest electrophilic aromatic substitution. Draw detailed mechanisms with resonance structures to illustrate your reasoning. (10 pts.)
5. Starting from benzene, propose efficient synthetic routes for the two transformations shown below. As additional organic starting materials, you may use *any alcohol or acid chloride containing 4 carbons or fewer*. You may use any inorganic reagents you require. Assume that different isomers can be separated.

For each synthesis, **clearly indicate** your final synthetic route (Work backwards!) (21 pts.)

(a) \[ \text{C}_6\text{H}_6 \xrightarrow{?} \text{C}_6\text{H}_5\text{Br} \]

(b) \[ \text{C}_6\text{H}_6 \xrightarrow{?} \text{C}_6\text{H}_5\text{CH}CH_2\text{CH}_2\text{OH} \]
6. In boxes 1-6, fill in the missing reagent(s). Draw the structure of the final product in the last box. (11 pts.)

[Diagram of chemical reactions and structures]