Organic Chemistry II (CHE 232–002)
Examination I
March 1, 2007

Name (Print legibly): __________ KEY __________
(last) (first)

Student ID#: _________________________________

PLEASE observe the following:
You are allowed to have scratch paper (provided by me), and a simple model set. **You do not need a calculator.** Please have your student ID card present on your desk. Read through the entire exam before beginning and start first on the problems that seem easiest to you. Please provide clear and concise answers to the questions in the area provided, the back of an exam page, or on the clearly labeled spare page.

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<td>6a-d</td>
<td>_____/16</td>
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Total: _____/
TABLE OF ATOMIC WEIGHT MULTIPLES.

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<td>C=C–C–H, O=C–C–H, C=C–H</td>
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<td>X–C–H, X=O, N, S, Hal</td>
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<tr>
<td>C=C–H, RX2C–H</td>
<td>4.5-6.5</td>
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<td>aryl H</td>
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<td>O=C–H</td>
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1. (10 pts) Which of the following species is/are aromatic? (Circle the aromatic species)

Aromatic species are shown in red.
2. (10 pts) Enter the letter of the best answer in the space provided.

_c__ (a) Which of the following compounds would you expect to be the most reactive toward ring nitration?

a. Benzene   d. p-Xylene
b. Toluene   e. Benzoic acid
c. m-Xylene

c__ (b) This molecule cannot participate as a reactant in a Friedel-Crafts reaction.

a. Benzene   d. Toluene
b. Chlorobenzene   e. t-Butylbenzene
c. Nitrobenzene

_a__ (c) Undesired polysubstitution of an aromatic ring is most likely to be encountered in the case of

a. Friedel-Crafts alkylation   d. Sulfonation
b. Friedel-Crafts acylation   e. Chlorination
c. Nitration

e__ (d) Which of the following electrophilic aromatic substitution reactions is reversible?

a. Friedel-Crafts acylation   d. Nitration
b. Chlorination   e. Sulfonation
c. Nitration
3. (4 points each, 52 points total). Draw products of the reactions below. If no reaction occurs, write N.R.

(a) \[
\begin{align*}
\text{Br}_2 & \quad \rightarrow \quad \text{N.R.} \\
\end{align*}
\]

(b) \[
\begin{align*}
\text{HNO}_3/\text{H}_2\text{SO}_4 & \quad \rightarrow \quad \text{O}_2\text{N-CH}_3 + \text{C}_6\text{H}_4\text{CH}_3
\end{align*}
\]

(c) \[
\begin{align*}
\text{Cl}_2 & \quad \rightarrow \quad \text{C}_6\text{H}_4\text{Cl}
\end{align*}
\]

(d) \[
\begin{align*}
\text{CH}_3\text{Cl} & \quad \rightarrow \quad \text{N.R.}
\end{align*}
\]

(e) \[
\begin{align*}
\text{H}_3\text{C-CH}_2\text{NO}_2 & \quad \rightarrow \quad \text{H}_3\text{COO-CH}_2\text{CH}_2\text{NO}_2
\end{align*}
\]

(f) \[
\begin{align*}
\text{OH}^- & \quad \text{reflux (heat)} \quad \rightarrow \quad \text{C}_6\text{H}_4\text{COO}^-
\end{align*}
\]

(g) \[
\begin{align*}
\text{OCH}_3 & \quad \rightarrow \quad \text{OCH}_3
\end{align*}
\]

(h) \[
\begin{align*}
\text{Br}_2 & \quad \text{excess} \quad \rightarrow \quad \text{Br}_2
\end{align*}
\]
(i) $NO_2$ $\xrightarrow{Br_2, FeBr_3}$ $NO_2$ $\xrightarrow{Sn, HCl}$ $NH_2$

(j) $NO_2$ $\xrightarrow{SO_3, H_2SO_4}$ $NO_2$ $\xrightarrow{OCH_3}$ $SO_3H$

(k) $Br$ $\xrightarrow{MeNHET. Bu^ONa, Pd(0), phosphine}$ $H_3C$ $\xrightarrow{NMeEt}$

(l) $CH_3$ $\xrightarrow{Pd(0), phosphine}$ $H_3C$
4. (12 points) Draw a mechanism, using arrows, for the reaction of chlorobenzene with nitric acid in concentrated sulfuric acid. First, show the mechanism for the formation of the electrophile then show the mechanism when the electrophilic attack is at the \textit{para} position. Show all possible resonance forms of the arenium ion formed by \textit{para} attack. Include the final step of conversion of the arenium ion to the product in your mechanism.
5. (12 points) Starting from benzene, show how you would make compounds 1 and 2 cleanly in more than one step. Note: a clean reaction essentially produces only one product. There is no need to show mechanisms for this question.

(a) 

Several approaches possible including:

(b) 

Several approaches possible including:
6. (16 pts) In each problem below, choose one method (optical activity, MS, IR, \(^{1}\)H NMR, or \(^{13}\)C NMR) that will allow you to unambiguously distinguish between the two compounds. Precisely describe the difference that you expect to see in the spectra of the two compounds that will allow you to distinguish between the compounds (correct description of the difference in the spectra is worth 3 points). Be brief (no more than two sentences).

(a)

Method for distinguishing:

\(^{1}\)H NMR

Difference:

A will show two singlet resonances in the aromatic region of its spectrum while B will show two doublet resonances in the aromatic region of its \(^{1}\)H NMR spectrum.

(b)

Method for distinguishing:

Mass spectrometry

Difference:

C and D have different molar masses hence and hence can be differentiated on the basis of the \(M^+\) ion observed. Also, C will show a peak for its [M+2]\(^{+}\) ion whose intensity is 33% that of the \(M^+\) ion while D will show a peak for its [M+2]\(^{+}\) whose intensity is equal to that of the \(M^+\) ion.
Method for distinguishing:

\(^1\)H NMR and/or proton-coupled \(^{13}\)C NMR

Difference:

The \(^1\)H NMR spectrum of E will show two triplet resonances in 1:1 integral ratio for its two chemically inequivalent methylene (CH\(_2\)) units while the \(^1\)H NMR spectrum of F will show a doublet- and a quartet resonance in 3:1 integral ratio for its methyl and methine protons, respectively.

Proton-coupled \(^{13}\)C NMR will similarly show two triplet resonances for the two chemically inequivalent methylene carbons in E while a quartet- and doublet resonance will be observed for methyl and methine carbons of F, respectively.

(Note: both compounds should the same number of resonances for phenyl protons and carbons)

(d) A compound has the formula C\(_8\)H\(_9\)Br. Its \(^1\)H NMR spectrum consists of a 3-hydrogen doublet at 2.0 ppm, a 1-hydrogen quartet at 5.15 ppm, and a 5-hydrogen multiplet at 7.35 ppm. Which is a possible structure for the compound? Assign the \(^1\)H NMR data.

- the aromatic hydrogens show at 7.35 ppm
7. (8 points) A compound of molecular formula $\text{C}_{15}\text{H}_{24}\text{O}$ has the spectral data below. Deduce a reasonable structure for the compound and briefly explain how the given data is consistent with your proposed structure.

- Mass spectrum: $m/z = 220, 205, 57$; IR (Nujol): 3660 cm$^{-1}$ (m, sharp).
- $^1\text{H NMR (CDCl}_3\text{)}$: $\delta$ 1.43 (s, 18H), 2.27 (s, 3H), 5.00 (s, 1H), 6.98 (s, 2H).  [Signal multiplicity and number of protons shown in parenthesis]
- $^{13}\text{C NMR (CDCl}_3\text{)}$: $\delta$ 21.2 (q), 30.4 (q), 34.2 (s), 125.5 (d), 128.2 (s), 135.8 (s), 151.5 (s)

The two structures most consistent with the above data are:

The mass spectral data is consistent with the molecular formula and suggest the presence of methyl (220–205 = 15) and butyl ($\text{C}_4\text{H}_{9}$, mass = 57) fragments in the compound.

The IR data is consistent with presence of an OH group.

In the $^1\text{H NMR}$ data, the singlet resonance at 6.98 ppm, which integrates as two protons, indicates that there are two aromatic hydrogens and that they are chemically equivalent. The singlet at 2.27 ppm, which integrates as three protons, is in consistent with a $\text{CH}_3$ bound to an aryl group. How do we account for the singlet at 1.43 ppm, which represents 18H? This peak is found in the region where saturated alkyl protons show. Clearly, observation of a singlet resonance shows that the hydrogens are chemical equivalent and that there aren’t any chemically inequivalent hydrogens within 2– or 3 bonds of them. These hydrogens can be accounted for by two t-butyl groups bound to the phenyl ring with identical connectivity (remember the mass spectral data?). This leaves the peak at 5.00 as the OH proton. As shown above, there are two different ways we can distribute the groups around the phenyl ring.

In the proton-coupled $^{13}\text{C NMR}$ spectrum, t-butyl group $\text{CH}_3$’s show as a quartet at 21.2 ppm, the quaternary carbon ($-\text{CMe}_3$) shows a singlet at 34.2 ppm, the ring-bound $\text{CH}_3$ shows a quartet at 30.4 ppm. In either structure, there are four different types of phenyl carbons hence the four downfield resonances; the doublet at 125.5 ppm is clearly due to the
two carbon atoms that have a hydrogen atom bound to them; the fact that these are the most shielded aromatic carbon atoms suggest that these carbon atoms are not adjacent to the carbon bearing the electron with drawing alcohol group and favors structure A. The singlet at 151.5 ppm is due to the carbon with the OH group bound to it.