Chemistry 341

Exam 2
October 24, 2000

Dr. McMahon

This exam consists of 10 questions on 9 pages.

In addition, a periodic table is included at the end of the exam.

Print Name ___________________________  Grading Key

<table>
<thead>
<tr>
<th>Circle your TA's name</th>
<th>Grading</th>
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<tbody>
<tr>
<td>Wendy de Prophetis</td>
<td>1. _____ / 12</td>
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<td>Sarah Maifeld</td>
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<td>Melissa Feenstra</td>
<td>2. _____ / 9</td>
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<td>Meg Schmitt</td>
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<td>Gina Gencarelli</td>
<td>3. _____ / 20</td>
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<td>John Stevens</td>
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<td>Lisa Jungbauer</td>
<td>4. _____ / 10</td>
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<td>Circle the day and time</td>
<td>5. _____ / 6</td>
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<td>of your Discussion Session</td>
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<td>10. _____ / 6</td>
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Total _____ / 100
(12 pts) 1. The following questions pertain to the $S_N2$ reaction. Indicate your answer by circling the appropriate response.

(a) Both the alkyl halide and the nucleophile are involved in the transition state for the rate determining step.

(b) Reaction proceeds with inversion of configuration at the substitution center.

(c) Reaction proceeds with loss of optical activity.

(d) The order of reactivity is tertiary $>$ secondary $>$ primary.

(e) The greater the nucleophilicity of the nucleophile, the greater the rate of reaction.

(f) The nucleophile must have an unshared pair of electrons and bear a negative charge.

(9 pts) 2. Disparlure, a sex attractant of the gypsy moth, has been synthesized in the laboratory from the following (Z)-alkene.

(Z)-2-Methyl-7-octadecene

[Diagram of the (Z)-2-Methyl-7-octadecene molecule with an arrow indicating the conversion to Disparlure, which is structurally similar but with the addition of a functional group.

(a) What reagent(s) would you use to convert the (Z)-alkene to disparlure?

(b) How many stereoisomers are possible for disparlure? $2^2 = 4$

(c) How many stereoisomers would be formed using the reaction conditions that you specified in part (a)?

racemic mixture
(20 pts) 3. Draw structures for the major organic products of the following reactions. (It is not necessary to write a balanced reaction with respect to reagents and inorganic products.)

(a) \[
\text{Cyclohexanol} \quad \text{Na metal} \quad \text{Cyclohexyl} \quad \text{Na}^+ \quad (+2 p\text{t for each})
\]

(b) \[
\text{Cyclohexanol} \quad \text{SOCl}_2 \quad \text{Cyclohexyl} \quad \text{Cl}^{-} 
\]

(c) \[
\text{Cyclohexanol} \quad \text{CrO}_3 \quad \text{aq. H}_2\text{SO}_4, \text{acetone} \quad \text{Cyclohexyl} \quad \text{OH} \quad (+1 pt for aldehyde)
\]

(d) \[
\text{Cyclohexanol} \quad \text{PCC} \quad \text{CH}_2\text{Cl}_2 \quad \text{PCC = pyridinium chlorochromate} \quad \text{Cyclohexyl} \quad \text{+H}^+ \quad (+1 pt for acid)
\]

(e) \[
\text{Cyclohexanol} \quad 1) \text{NaH} \quad 2) \text{CH}_3\text{I} \quad \text{Cyclohexyl} \quad \text{O}^{-} \quad (+1 pt for each)
\]

(f) \[
\text{Benzene} \quad \text{HNO}_3 \quad \text{H}_2\text{SO}_4 \quad \text{Cyclohexyl} \quad \text{NO}_2 \quad \text{O}_2\text{N}^{-} \quad (+1 pt each)
\]

(g) \[
\text{Benzene} \quad \text{Br}_2 \quad \text{FeBr}_3 \quad \text{Cyclohexyl} \quad \text{Br}^{-} \quad \text{Br}^{-} \quad (+1 pt each)
\]

(h) \[
\text{Benzene} \quad \text{CH}_3\text{Cl} \quad \text{AlCl}_3 \quad \text{Cyclohexyl} \quad \text{NO}_2 \quad (+1 pt for alkylation, but wrong regiochemistry)
\]

(i) \[
\text{Benzene} \quad 1) \text{CH}_3\text{CH}_2\text{Li} \quad 2) \text{H}_3\text{O}^+ \quad \text{Cyclohexyl} \quad \text{OH} \quad (+1 pt for either answer)
\]

(j) \[
\text{Benzene} \quad \text{(CH}_3\text{)}_3\text{CO}^- \quad \text{Cyclohexyl} \quad \text{(CH}_3\text{)}_3\text{CO}^- \quad (+1 pt for either answer)
\]


full credit for either answer

don't need to have both
(10 pts) 4. Treatment of 1-methylcyclohexene with methanol in the presence of a sulfuric acid catalyst gives a compound of molecular formula C₈H₁₆O.

\[ \text{C}_8\text{H}_16\text{O} \]

(a) Propose a structural formula for the product.

+4 pts

(b) Provide a detailed mechanism for the reaction.

+6 pts correct
+4 pts OK but mistakes
+2 pts so=so
+0 pts WRONG or blank

2 pts for carbocation \*
(6 pts) 5. (a) Label the stereogenic centers in cholesterol with asterisks (*).

8 stereogenic centers
+1 pt for each correct assignment
-1 pt for each incorrect assignment
(zero is lowest possible score - no negative scores)

(b) How many stereoisomers are possible for this molecule?

+2 pts full credit in part (b)
if answer is consistent with # stereogenic centers in part (a)

(6 pts) 6. Indicate the starting material that you would use in the following reactions to afford the given product in high yield and uncontaminated with isomeric products.

+2 pts each

(a) \[
\begin{align*}
\text{(CH}_3\text{)}_3\text{CO} & \xrightarrow{} \\
x = \text{Cl}, \text{Br}, \text{I}
\end{align*}
\]

(b) \[
\begin{align*}
\text{(CH}_3\text{)}_3\text{CO} & \xrightarrow{} \\
x = \text{Cl}, \text{Br}, \text{I}
\end{align*}
\]

(c) \[
\begin{align*}
\text{OH} & \quad \text{HO} \\
\text{aq. H}_2\text{SO}_4 \quad \text{acetone}
\end{align*}
\]

\[
\begin{align*}
\text{CrO}_3 & \xrightarrow{} \\
\text{O} & \quad \text{O}
\end{align*}
\]
(10 pts) 7. The following ketone, isolated from the roots of several members of the iris family, has an odor like that of violets and is used as a fragrance in perfumes. Show how you would synthesize this molecule, starting from benzene. You may use any other reagents, organic or inorganic. Draw the structures of any intermediate compounds that would be isolated, and specify all reagents and reaction conditions. (It is not necessary to write out every intermediate in a reaction mechanism.)

![Chemical structures and reactions]

- These are the most likely answers, given the material we have covered to date.
- Other correct answers are possible.

+10 pts correct
+7 pts ok, but errors (i.e. reversing the order of reactions will give wrong product)
+4 pts so-so
+0 pts wrong or blank
(12 pts) 8. (a) For centuries, Chinese herbal medicine has used extracts of the plant *Ephedra sinica* to treat asthma. Ephedrine, a potent dilator of the air passages of the lungs, has been isolated from this plant. The naturally occurring stereoisomer is levorotatory and has the following structure. Assign the absolute configuration (*R* or *S*) at each stereogenic center.

(b) The specific rotation of ephedrine, \([\alpha]_D\), is \(-41^\circ\).
What is the specific rotation of its enantiomer? \( +41^\circ \)  

(c) What is the stereochemical relationship between ephedrine and the following structure?

- identical enantiomers
- diastereomers  

(circle)  

\[
\begin{array}{c}
\text{Ephedrine} \\
\text{Same configuration}
\end{array}
\]  

\[
\begin{array}{c}
\text{opposite configuration}
\end{array}
\]
9. Use the given compound numbers to rank the following compounds in order of decreasing acidity. (Remember that "decreasing acidity" is the same as "increasing basicity").

(a) $\text{H}_3\text{CO}$ 1 $\text{O}_2\text{N}$ 2 3

\[
2 > 3 > 1
\]

strongest acid weakest acid

+1 pt for strongest acid

(b) $\text{H}_2\text{O}$ 1 $\text{NH}_3$ 2 $\text{HBr}$ 3

\[
3 > 1 > 2
\]

strongest acid weakest acid

+1 pt for strongest acid

(c) $\text{OH}$ 1 $\text{C}_2\text{H}_2\text{CH}$ 2 $\text{O}$ 3

\[
1 > 3 > 2
\]

weakest base strongest base

+1 pt for strongest base
Cyclohexene reacts with Br₂ to give an addition product. Benzene doesn't react with Br₂ unless a Lewis Acid catalyst is used (e.g. FeBr₃), and these conditions give a substitution product. 

BRIEFLY explain the reason for the difference in reactivity. (It is not necessary to write reaction mechanisms to explain your answer.)

Benzene has special stability associated with cyclic, conjugated π electrons ("aromaticity").

Any addition reaction would disrupt aromaticity

⇒ not observed

Substitution reactions are therefore observed for aromatic compounds, so that aromaticity is retained.

(Looking for an explanation of this general type.)