Midterm #2

Ian R. Gould

PRINTED FIRST NAME ___________ PRINTED LAST NAME ___________

complete this section

Person on your LEFT (or Empty or Aisle) ___________________________________

Person on your RIGHT (or Empty or Aisle) _________________________________

ASU or Posting ID ______________________________________________________

Room you are supposed to take this test in (LS A-191 for onground and PS H-152 for hybrid)

PRINT YOUR NAME ON EACH PAGE!
READ THE DIRECTIONS CAREFULLY!
USE BLANK PAGES AS SCRATCH PAPER
work on blank pages will not be graded...
WRITE CLEARLY!
MOLECULAR MODELS ARE ALLOWED
DO NOT USE RED INK
DON'T CHEAT, USE COMMON SENSE!

Interaction Energies, kcal/mol

<table>
<thead>
<tr>
<th>Eclipsing</th>
<th>Gauche</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/H</td>
<td>~1.0</td>
</tr>
<tr>
<td>H/Me</td>
<td>~1.4</td>
</tr>
<tr>
<td>Me/Me</td>
<td>~2.6</td>
</tr>
<tr>
<td>Et/Me</td>
<td>~0.95</td>
</tr>
<tr>
<td>i-Pr/Me</td>
<td>~1.1</td>
</tr>
<tr>
<td>t-Bu/Me</td>
<td>~2.7</td>
</tr>
</tbody>
</table>

Infrared Correlation Chart

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>N–H</th>
<th>O–H</th>
<th>C=O</th>
<th>C–N</th>
</tr>
</thead>
<tbody>
<tr>
<td>3200–3600</td>
<td>broad with spikes ~3300</td>
<td>3500–3100</td>
<td>2700–2820</td>
<td>2500–3000</td>
</tr>
</tbody>
</table>

NMR Correlation Charts

<table>
<thead>
<tr>
<th>δ (ppm)</th>
<th>Aromatic Ar–H</th>
<th>Alkyl 3' &gt; 2' &gt; 1'</th>
<th>Aromatic 3' &gt; 2' &gt; 1'</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>R–O–H</td>
<td>R–C–H</td>
<td>R–C=N</td>
</tr>
<tr>
<td>10</td>
<td>R–C–OH</td>
<td>R–C=N</td>
<td>R–C=N</td>
</tr>
<tr>
<td>9</td>
<td>R–C–OH</td>
<td>R–C=N</td>
<td>R–C=N</td>
</tr>
<tr>
<td>8</td>
<td>R–C–OH</td>
<td>R–C=N</td>
<td>R–C=N</td>
</tr>
<tr>
<td>7</td>
<td>R–C–OH</td>
<td>R–C=N</td>
<td>R–C=N</td>
</tr>
<tr>
<td>6</td>
<td>R–C–OH</td>
<td>R–C=N</td>
<td>R–C=N</td>
</tr>
<tr>
<td>5</td>
<td>R–C–OH</td>
<td>R–C=N</td>
<td>R–C=N</td>
</tr>
<tr>
<td>4</td>
<td>R–C–OH</td>
<td>R–C=N</td>
<td>R–C=N</td>
</tr>
<tr>
<td>3</td>
<td>R–C–OH</td>
<td>R–C=N</td>
<td>R–C=N</td>
</tr>
<tr>
<td>2</td>
<td>R–C–OH</td>
<td>R–C=N</td>
<td>R–C=N</td>
</tr>
<tr>
<td>1</td>
<td>R–C–OH</td>
<td>R–C=N</td>
<td>R–C=N</td>
</tr>
<tr>
<td>0</td>
<td>R–C–OH</td>
<td>R–C=N</td>
<td>R–C=N</td>
</tr>
</tbody>
</table>

\( R \rightarrow \text{NH}_2, \text{variable and condition dependent}, \text{ca.} 2 \cdot 6 \delta \)
Question 1 (12 pts.) Give the IUPAC name for the following compound. Be sure to use cis/trans, E/Z or R/S where appropriate.

(4R)-methoxyhexan-(3S)-ol
(4R)-methoxy-(3S)-hexanol
e.tc.
-1pt each error, do not propagate errors

Question 2 (20 pts.) Show how you would make the target compound on the right from the starting compound on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. Ignore stereochemistry.

Extra Credit Question (5 pts.) In which kind of biomolecule can a photochemical 2 + 2 cycloaddition reaction take place

DNA          phospholipid          carbohydrate          protein
Question 3 (16 pts) Give the major organic products of the following reactions, indicate the stereochemistry using wedged/dashed bonds as appropriate and be sure to indicate the presence of any racemic mixtures.

(a) 
\[ \text{Br} \]
1. Na\(^+\) – O-t-Bu
2. MCPBA
3. MeOH/HCl

(b)
\[ \text{Me} \]
\[ \text{Me} \]
\[ \text{EtOH} \]
Na\(^+\) – OEt
EtOH

Question 4 (9 pts) Give the major organic product of the following reaction, indicate the stereochemistry using wedged/dashed bonds as appropriate and be sure to indicate the presence of any racemic mixtures. **State whether a solution of the product(s) would be optically active or not, with a very brief explanation.**

\[ \text{H}_2\text{N} \]
\[ \text{H}_2\text{N} \]
heat

Question 5 (8 pts) Give the diene and dienophile that react to give the provided structure in a Diels-Alder reaction.

\[ \text{OMe} \]
\[ \text{OMe} \]
heat

Question 6 (12 pts)
(a) Give the curved arrow-pushing for the following electrocyclic ring opening reaction

(b) How many electrons are involved in the reaction? 4

d) Will the ALLOWED reaction proceed via conrotatory or disrotatory ring opening? conrotatory
Question 7 (24 pts.)
a) provide a curved arrow-pushing mechanism for formation of both products of the following
reaction, indicate the Lewis acid/base at each step, LA/LB, and whether they are also Bronsted
carids/bases, BA/BB. Show all important resonance contributors for the intermediates.

```
OH
HCl (cat.)
EtOH (solvent)
OEt

LA/BA
LB/BB

HOH
Et
O

LA/BA
LB/BB

A

OEt

B

LA/BA
LB/BB
```
c) Indicate which product would be formed under conditions of kinetic control and which would
be formed under conditions of thermodynamic control, AND, which would be the major product
at high temperatures AND at low temperatures, give a BRIEF explanation

at high temperatures the reactions are reversible and the thermodynamic product would be the
major product, at low temperature the reactions are irreversible and the kinetic product would be
the major
Question 8 (20 pts.) Show how you would make the target compound on the right from the starting compound on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.

Question 9 (18 pts.) Several of the C-C bonds in the provided structure can be made in a Grignard reaction. For TWO OF THESE C-C BONDS, provide the Grignard reagent AND the structure it would react with (assume an acid workup step. i.e. do not include the H$_3$O$^+$), and CLEARLY INDICATE WITH AN ARROW WHICH C-C bond you are making in each reaction.
Question 10 (18 pts) The following cation undergoes an electrocyclic ring closure reaction.

\[
\begin{align*}
&\text{H}_3\text{C} \quad \text{CH}_3 \\
&\text{CH}_3 \quad \text{H}_3\text{C} \\
&\text{H}_3\text{C} \quad \text{CH}_3
\end{align*}
\]

heat

\[
\begin{align*}
&\text{H}_3\text{C} \quad \text{CH}_3 \\
&\text{H}_3\text{C} \\
&\text{H}_3\text{C} \\
&\text{H}_3\text{C} \quad \text{CH}_3
\end{align*}
\]

- or -

these are resonance contributors

a) Give the curved arrow-pushing and the product of the reaction, and indicate whether the product is achiral, a racemic mixture or a meso compound.
b) Draw the HOMO of the reactant on TOP OF THE STRUCTURE below.
c) Does the allowed reaction proceed via a conrotatory or a disrotatory ring closure? Conrotatory.

Question 11 (18 pts.) In this question you are going to work out whether the reaction SHOWN would be allowed or forbidden based on the rules for pericyclic reactions.

For this reaction........

\[
\begin{align*}
&\text{H}_2\text{C} \quad \text{A} \\
&\text{H}_2\text{C} \\
&\text{H}_2\text{C} \quad \text{N} \\
&\text{A} \quad \text{B}
\end{align*}
\]

heat

\[
\begin{align*}
&\text{H}_2\text{C} \quad \text{B} \\
&\text{H}_2\text{C} \quad \text{H}_2\text{C} \\
&\text{H}_2\text{C} \\
&\text{H}_2\text{C} \quad \text{H}_2\text{C}
\end{align*}
\]

a) Draw the arrow-pushing to account for the bond breaking/making.
b) Draw the HOMO of reactant A on TOP of the structure re-drawn for you here.
c) Draw the LUMO of reactant B on TOP of the structure re-drawn for you here.
d) Would an ALLOWED reaction between these two species be suprafacial/suprafacial or suprafacial/antarafacial? suprafacial/antarafacial.
e) Would an ALLOWED reaction between these two species proceed via a Huckel or a Mobius transition state? Möbius.
f) Assuming the reaction is SUPRAFACIAL for reactant A, is THE REACTION SHOWN above allowed or forbidden? Allowed.