## Exam 2

February 27, 2013
Organic Chemistry 335

## Please Sit Every Other Seat

This exam is 65 minutes long (9-10:05). I will post a key on D2L when all the exams are in. There will be no make-up exams. Please be considerate of your fellow classmates when leaving. Don't stand by the doors and discuss the exam.

All cell phones and personal audio devices must be turned off and put away. The use of calculators, notes, the textbook, or your neighbors test is not permitted during the exam. You may use molecular models, but they cannot be shared during the exam.

Please put your in-class number and your name on the second page and back of the exam.
You may tear off this page for easier use of the tables.
If your test becomes unstapled, please let me know

| IR Data |  | $\begin{array}{cc} \text { General } \\ \text { Shape } & \left(\begin{array}{l} \text { intensity } \\ \text { strong }=s \\ \text { middle }=m \\ \text { weak }=w \end{array}\right) \end{array}$ |
| :---: | :---: | :---: |
| O-H alcohol | 3600-3200 | broad ( $\mathrm{s} / \mathrm{m}$ ) |
| O-H Carboxylic Acid | 3600-2500 | broad ( $\mathrm{s} / \mathrm{m} / \mathrm{w}$ ) |
| N-H Amine/Amide | 3500-3350 | 'fangs" (s/m/w) |
| sp C-H | 3320-3310 | sharp ( $\mathrm{s} / \mathrm{m} / \mathrm{w}$ ) |
| $\mathrm{sp}^{2} \mathrm{C}-\mathrm{H}$ | 3100-3000 | $\operatorname{sharp}(\mathrm{s} / \mathrm{m} / \mathrm{w})$ |
| sp ${ }^{3} \mathrm{C}-\mathrm{H}$ | 3000-2900 | sharp (s/m) |
| $-\mathrm{C} \equiv \mathrm{N}$ nitrile | 2240-2280 | sharp ( $\mathrm{w} / \mathrm{m} / \mathrm{s}$ ) |
| $-\mathrm{C} \equiv \mathrm{C}$ sp-sp alkyne | 2100-2200 | sharp (m) |
| - $\mathrm{C}=\mathrm{O}$ (carbonyl) | 1750-1650 | sharp (s) |
| $-\mathrm{C}=\mathrm{C} \mathrm{sp}^{2}-\mathrm{sp}^{2}$ | 1680-1600 | $\boldsymbol{s h a r p}(\mathrm{m} / \mathrm{w})$ |
| $-\mathrm{sp}^{2} \mathrm{C}-\mathrm{O}$ | 1250-1200 | $\boldsymbol{\operatorname { s h a r }}(\mathrm{m} / \mathrm{w})$ |
| -sp ${ }^{3} \mathrm{C}-\mathrm{O}$ | 1200-1025 | $\operatorname{sharp}(\mathrm{m} / \mathrm{w})$ |


| ${ }^{13}$ C NMR Chemical Shift Ranges |  |
| :---: | :---: |
| Type of Carbon | Chemical Shift ( $\delta$ ) range in ppm |
| $\mathrm{RCH}_{3}$ | 0 to 35 |
| $\mathrm{R}_{2} \mathrm{CH}_{2}$ | 15 to 40 |
| $\mathrm{R}_{3} \underline{\mathrm{C}} \mathrm{H}$ | 25 to 50 |
| $\mathrm{R}_{4} \mathbf{C}$ | 30 to 40 |
| $\mathrm{R} \mathbf{C}=\underline{\mathbf{C}} \mathrm{R}$ | 65 to 90 |
| $\mathrm{R}_{2} \mathbf{C}=\mathbf{C R}_{2}$ | 100 to 150 |
| (1) | 110 to 175 |
| RCHBr | 20 to 40 |
| RCHBr | 20 to 40 |
| RCHCl | 25 to 50 |
| $\mathrm{RCH}_{2} \mathrm{NH}_{2}$ | 35 to 50 |
| $\begin{aligned} & \mathrm{R}_{\mathbf{C H}}^{2} \\ & \mathrm{R} \mathbf{O H} \\ & \mathrm{R} \underline{\mathbf{C}} \mathrm{H}_{2} \mathrm{OR} \end{aligned}$ | 50 to 65 |
| $\mathrm{RC}=\mathrm{N}$ | 110 to 125 |
|  | 160 to 185 |
| $\begin{array}{cc} \mathrm{O} & \mathrm{O} \\ \mathrm{II} \\ \mathrm{R} \\ \mathrm{R} \\ \hline \underline{\mathrm{C}} \mathrm{R} \end{array}$ | 190 to 220 |


| Predicting the chemical shift <br> of proton/s on a sp ${ }^{3}$ carbon <br> in a ${ }^{1} \mathrm{H}$ NMR spectrum <br> methyl $\left(\mathrm{XCH}_{3}\right)$ : starting point is 0.9 ppm . methene $\left(\mathrm{X}_{2} \mathrm{CH}_{2}\right)$ : starting point is 1.3 ppm . methine $\left(\mathrm{X}_{3} \mathrm{CH}\right)$ : starting point is 1.5 ppm |  |
| :---: | :---: |
| Group (X) | Increment (ppm) |
| $\xi-\mathrm{CH}_{3}$ (or any alkyl group) | 0.0 |
| $\zeta-\mathrm{CH}=\mathrm{CH}_{2}$ (or an alkene group) | 0.9 |
| $\begin{gathered} \text { \}-C } \equiv \mathrm{CH} \text { \}-C } \equiv \mathrm{CR} \\ \text { (an alkyne group) } \end{gathered}$ | 0.9 |
| $\}$-SH, $\}$-SR | 1.2 |
|  | 1.2 |
| $\}-\mathrm{C} \equiv \mathrm{N}$ | 1.2 |
| $\left.\xi-\mathrm{NH}_{2}, \xi \mathrm{NHR}\right\}-\mathrm{NR}_{2}$ | 1.2 |
| $\}-\mathrm{I}$ | 1.3 |
| $\xi-\mathrm{Ph} \geqslant \square$ | 1.4 |
| $\}-\mathrm{Br}$ | 1.8 |
| $\}-\mathrm{Cl}$ | 2.1 |
| $\}-\mathrm{OH}$ \}-OR | 2.4 |
| $\stackrel{O}{\mathrm{O}}_{\mathrm{O}}^{\mathbb{H}_{R}}$ | 2.8 |
| S-O- | 3.0 |
| $\}-\mathrm{F}$ | 3.2 |


| ${ }^{1}$ H NMR Chemical Shift Ranges for $H$ attached to non $\mathbf{s p}^{\mathbf{3}}$ Carbons |  |
| :---: | :---: |
| Type of Proton | Chemical Shift ( $\delta$ ) range in ppm |
| $\begin{gathered} \hline \mathrm{O} \\ \text { RC̈O-H } \end{gathered}$ | 10 to 12 |
| $\begin{gathered} \text { O} \\ \text { RC- } \end{gathered}$ | 9 to 10 |
| - | 6.5 to 8.5 |
| $\underset{\substack{\text { C }}}{\substack{\text { C }}}$ | 4.5 to 5.5 |
| $\mathrm{RC} \equiv \mathrm{C}-\underline{\mathbf{H}}$ | 2 to 3 |
| $\mathrm{R}_{2} \mathrm{CO}-\underline{\mathrm{H}}$ | 1 to 5.5 |
| $\mathrm{R}_{2} \mathrm{CHN}-\mathrm{H}$ | 1 to 4 |

Organic Chemistry 335
Exam 2
February 27, 2013

In-class \# $\qquad$

Name
(Last, First)

1. Name the following compounds (10 points)


2. Draw, in bond line, an ester with the chemical formula $\mathrm{C}_{9} \mathrm{H}_{18} \mathrm{O}_{2}$ that would only have 5 peaks in a ${ }^{13} \mathrm{C}$ NMR ( 3 pts )
3. What was the starting material, reagents, or product/s for the following chemical transformations? If there is no reaction write "no reaction" Do not forget about stereochemistry (40 points)






4. Continued.


\&








5. Draw the complete mechanism of taking propan-2-ol to acetone using the premade chlorodimethylsulfonium species in a Swern oxidation. (11 points)

6. Design a racemic synthesis of 2-isopropyl-1-methylcyclohexanol. (10 points)

* The synthesis must start with cyclohexene.
* You can use any reaction you have learned this year.
* You may use any alcohol that has three carbons or less to add more carbons.
* You need to show the how you make the reagents and intermediate products.
* The major product must be carried on to the next step.
* You do not need to show the mechanisms.


6. What is the following $\mathrm{C}_{8} \mathrm{H}_{12} \mathrm{Cl}_{2} \mathrm{O}$ structure ?
(20 points: these 20 point are broken up in the problem)
What are the degrees of unsaturation or IHD? (3 point)


IR: 3082, 2959, 1721, $1627 \mathrm{~cm}-1$


List four types of bonds the IR show this molecule has. (4 points)
1.
2.
3.
4.

Please tell me what you think each peak in the ${ }^{1} H$ NMR represents
( $\mathrm{CH}_{\underline{x}}, \mathrm{OH}, \mathrm{NH}_{\underline{x}} \ldots$ ) and how you get its splitting pattern ( 6 points)
${ }^{1} \mathrm{H}$ NMR
$5.7(\mathrm{t}, 1 \mathrm{H})$
$5.4(\mathrm{t}, 1 \mathrm{H})$
3.5 (d, 2H)
3.0 (d, 2H)
1.8 (s, 3H)
1.7 (s, 3H)

## 6 Continued: Draw the structure that best fits all the data. (7 pts) Write ONLY ONE structure

7. Victor Drangirg attempted the following reactions to make compound X (see below). However, the reaction did not work. You do not need to worry about stereochemistry.
8. Mg, Dry $\mathrm{Et}_{2} \mathrm{O}$




7a. What is the problem with Victor reaction? (2 pts)

7b. Provide an alternative synthesis of compound X using a Grignard reagent. You may use any necessary reagents and use any reactions you have learned in 334 and 335. (4 pts)

Fill in the necessary reagents for the following reaction sequence.


