### Chemistry 30B Fall 2003

**MIDTERM #1 ANSWER KEY**

*(50 Min)*

Monday October 20th

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***DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO***

ONLY ANSWERS WRITTEN IN THE BOXES PROVIDED WILL BE GRADED

INTERPRETATION OF THE QUESTIONS IS PART OF THE EXAM – DO NOT ASK FOR THE QUESTIONS TO BE EXPLAINED TO YOU

"There is no fear in science greater than that of being wrong. But the scientist who cannot act in the face of that fear stands little chance of changing textbooks" - J Michael Bishop
Question 1 Each of these reactions produces ONE MAJOR PRODUCT. In each case, draw this product (including appropriate stereochemistry where relevant) in the box provided. For multi-step reactions just give the FINAL product, i.e., no intermediates. (2 points each)
(f) $\text{OH}$ \quad \xrightarrow{\text{(i) } \text{PBr}_3} \quad \text{SH}
\quad \xrightarrow{\text{(ii) } \text{NaSH}}

(g) $\text{I}$ \quad \xrightarrow{\text{(i) } \text{H}_2\text{N}^-\text{CH}_2\text{NH}_2} \quad \text{SH}
\quad \xrightarrow{\text{(ii) } \text{NaOH} / \text{H}_2\text{O}}

(h) $\text{CH}_3$ \quad \xrightarrow{\text{H}_2\text{SO}_4 \text{ (cat)}} \quad \text{O}

(i) $\text{OH}$ \quad \xrightarrow{\text{(i) } \text{MsCl} / \text{pyridine}} \quad \text{CN}
\quad \xrightarrow{\text{(ii) } \text{NaCN}}

(j) $\text{excess HI}$

(Extra Credit – 3 points)

$\text{Br}_2$ \quad \xrightarrow{\text{(i) } \text{Br}_2} \quad \text{I}
\quad \xrightarrow{\text{(ii) } \text{excess } \text{NaNH}_2}$
Question 2  Shown below are two short synthetic schemes, the one on the left results in the formation of compound \( \text{E} \) (molecular formula \( C_4H_8O \)), and the one on the right results in the formation of compound \( \text{J} \) (molecular formula \( C_3H_3Na \)). When \( \text{E} \) and \( \text{J} \) are reacted together (box at bottom of the page), 2-methyl-hex-4-yn-2-ol is formed. In the large boxes (\( \text{B, E, G, H, J} \)), fill in the structures of plausible intermediate compounds, and in the small boxes (\( \text{A, C, D, F, I} \)) fill in the reagents necessary to achieve each transformation. Note: \( \text{A, C, D, F and I} \) all correspond to single-step reactions – i.e., DO NOT write a multi-step synthesis in any of these boxes. (2 points per box)
Question 3  Deuterium (D) is a heavier isotope of hydrogen (H). Chemical reagents in which certain H atoms have been replaced by D are used to perform reactions in which the products are isotopically labeled. For each of the reactions below, draw the structure of the final product, CAREFULLY INDICATING the position of the D atoms in the products. (2 points each)

(a) \( \text{C} \equiv \text{C} \rightarrow (i) (\text{sia})_2\text{BH} \\
(ii) \text{AcOD} \)

(b) \( \text{C} \equiv \text{C} \rightarrow (i) (\text{sia})_2\text{BD} \\
(ii) \text{AcOH} \)

(c) \( \text{C} \equiv \text{C} \\
(i) \text{NaNH}_2 (ii) \text{D}_2\text{O} \\
(iii) (\text{sia})_2\text{BH} (iv) \text{AcOH} \)

(d) \( \text{C} \equiv \text{C} \) \( \text{D}_2 / \text{Lindlar} \)

(e) \( \text{C} \equiv \text{C} \\
(i) \text{NaNH}_2 (ii) \text{D}_2\text{O} \\
(iii) (\text{sia})_2\text{BD} (iv) \text{AcOH} \)

*Question 3 is continued on the next page...*
(f) \[
\text{[Equation]}
\]
\[
\text{(i) NaNH}_2 \text{ (ii) D}_2\text{O}
\]
\[
\text{(iii) (sia)}_2\text{BH (iv) AcOD}
\]

(g) \[
\text{[Equation]}
\]
\[
\text{(i) NaNH}_2 \text{ (ii) D}_2\text{O}
\]
\[
\text{(iii) D}_2 / \text{Lindlar}
\]

(h) \[
\text{[Equation]}
\]
\[
\text{(i) Lindlar / D}_2
\]
\[
\text{(ii) 3 atm H}_2 / \text{Pd catalyst}
\]

(i) \[
\text{[Equation]}
\]
\[
\text{3 atm D}_2 / \text{Pd catalyst}
\]

(j) \[
\text{[Equation]}
\]
\[
\text{(i) NaNH}_2 \text{ (ii) D}_2\text{O}
\]
\[
\text{(iii) 3 atm H}_2 / \text{Pd catalyst}
\]

(Extra Credit – 3 points)
Fill in the reagents necessary for this transformation

(i) NaNH\textsubscript{2}

(ii) CD\textsubscript{3}Br

(iii) Na / ND\textsubscript{3} (l)
Question 4  Propose a reasonable mechanism that accounts for the transformation shown in the box below. (10 points)
**Question 5** For each of the reactions below, draw the final product and indicate clearly any relevant stereochemistry. For each reaction, indicate whether a single non-meso compound (S), a racemic mixture (R), or a meso compound (M), is formed, by writing the appropriate letter (S, R or M) in the smaller box to the right. (3 + 1 points each)

(a) \[
\begin{align*}
\text{Cyclohexene} & \xrightarrow{\text{OsO}_4, \text{t-BuOOH}} \text{Product} \\
& \quad \quad \quad \quad \quad \quad \quad \text{M}
\end{align*}
\]

(b) \[
\begin{align*}
\text{Cyclohexene} & \xrightarrow{(i) \text{mCPBA}} \text{Product} \\
& \quad \quad \quad \quad (ii) \text{H}_2\text{O} / \text{H}^+ \\
& \quad \quad \quad \quad \quad \quad \quad \text{R}
\end{align*}
\]

(c) \[
\begin{align*}
\text{Cyclohexene} & \xrightarrow{(i) \text{mCPBA}} \text{Product} \\
& \quad \quad (ii) \text{MeOH} / \text{H}^+ \\
& \quad \quad \quad \quad \quad \quad \quad \text{R}
\end{align*}
\]

(d) \[
\begin{align*}
\text{Cyclohexene} & \xrightarrow{(i) \text{mCPBA}} \text{Product} \\
& \quad \quad (ii) \text{MeO}^-\text{Na}^+ \\
& \quad \quad (iii) \text{H}_2\text{O} \\
& \quad \quad \quad \quad \quad \quad \quad \text{R}
\end{align*}
\]

(e) \[
\begin{align*}
\text{Cyclohexene} & \xrightarrow{3 \text{ atm } \text{H}_2 / \text{Pd catalyst}} \text{Product} \\
& \quad \quad \quad \quad \quad \quad \quad \text{S}
\end{align*}
\]
Question 6  Using ONLY acetylene (C₂H₂) as your carbon source, and other NON-CARBON containing reagents you have encountered in Chem 30B thus far, propose a synthesis for 3-hexanone in the box below. Show all intermediates and reagents for each transformation (do not concern yourself with solvents). DO NOT SHOW MECHANISMS! (10 points)