CEM 850 Final Exam
December 11, 2018

This exam consists of 5 pages. Please make certain that your exam has all of the necessary pages. Total points possible for this exam are 150. In answering your questions, please write legibly and draw all structures clearly. Write all your answers in the exam booklets. Good luck.

I. Illustrate five of the following six “name reactions”. You do NOT need to provide arrow (electron) pushing mechanisms. (15 pts)

1. Babler oxidation
2. Barton-McCombie deoxygenation
3. Claisen condensation
4. Claisen rearrangement
5. Swern oxidation
6. An example of Umpolung

II. Provide a complete arrow (electron) pushing mechanism for the following transformations. (5 pts)

\[
\text{MgI} \quad \xrightarrow{1. \text{Et}_2\text{O}, \text{CO}_2} \quad \text{CO}_2\text{H}
\]

2. cat \text{HCl, H}_2\text{O}

III. Provide a complete arrow (electron) pushing mechanism for the following transformations. (5 pts)

\[
\text{I} \quad \xrightarrow{1. \text{NaCN, THF}} \quad \text{CO}_2\text{H}
\]

2. cat \text{HCl, H}_2\text{O}

IV. Provide a complete arrow (electron) pushing mechanism for the following transformation. (5 pts)

\[
\text{cat HCl, H}_2\text{O} \quad \xrightarrow{\text{cat HCl, H}_2\text{O}} \quad \text{O}
\]

V. Provide a complete arrow (electron) pushing mechanism for the following transformation. (5 pts)

\[
\text{cat HCl, H}_2\text{O} \quad \xrightarrow{\text{cat HCl, H}_2\text{O}} \quad \text{Keto}
\]
VI. Provide a complete arrow (electron) pushing mechanism for the following transformations. (10 pts)

\[
\begin{align*}
&\text{1. POCl}_3, \text{benzene, reflux, 3.5 h} \\
&\text{2. NaBH}_4, \text{MeOH, 1 h} \quad (50\% \, 2 \text{ steps})
\end{align*}
\]

VII. Provide a complete arrow (electron) pushing mechanism for the following transformation. Note: This process does NOT involve an S\text{N}2 reaction on B. (10 pts)

\[
\begin{align*}
\text{EtO} &\quad \text{EtO} \\
\text{O} &\quad \text{O}
\end{align*}
\]

VIIa. Provide a complete arrow (electron) pushing mechanism for the following transformations. (10 pts)

\[
\begin{align*}
\text{D} &\quad \text{Me} \\
\text{O} &\quad \text{Me}
\end{align*}
\]

VIIb. When the last step is run with LDA and allyl iodide the reaction affords D, which is a constitutional isomer of C. Propose a structure for D (not a mechanism explaining its formation). (3 pts)

IX. Provide a complete arrow (electron) pushing mechanism for the following transformation. Note the loss of the CHO group and the resultant stereochemistry. (10 pts)
X. Provide a complete arrow (electron) pushing mechanism for the following transformation. 
Note: This process involves a sigmatropic rearrangement. (10 pts)

\[ \text{MeO} \text{NMe}_2 \text{CO}_2\text{Me} \xrightarrow{\text{H}_3\text{C} \text{OMe} \text{MeO} \text{NMe}_2 \text{OMe}} \text{(5 equiv)} \xrightarrow{\text{xylene, reflux, 48 h}} \text{Me} \text{CO}_2\text{Me} \]

XI. Provide a complete arrow (electron) pushing mechanism for the following transformation. 
Note: This process does NOT involve a sigmatropic rearrangement (10 pts)

\[ \text{MeO} \text{BnO} \text{OMe} \text{H}_3\text{C} \xrightarrow{\text{MeO} \text{BnO} \text{NMe}_2 \text{OMe}} \text{(50%)} \]

XII. Provide a complete arrow (electron) pushing mechanism for the following transformation. 
Note: This process involves a formal [3+2] cycloaddition. (10 pts)

\[ \text{MeO} \text{BnO} \text{O} \text{Me} \text{O} \text{NMe}_2 \text{OH} \xrightarrow{\text{MeO} \text{BnO} \text{NMe}_2 \text{O}} \text{75%} \]

XIII. Provide a complete arrow (electron) pushing mechanism for the following transformations. 
(5 pts)

\[ \text{EtO}_2\text{C} \text{EtO}_2\text{SiEt}_3 \xrightarrow{1. \text{CO}_2\text{Et} 80^\circ\text{C} (87\%)} \text{EtO}_2\text{C} \text{EtO}_2\text{SiEt}_3 \xrightarrow{2. \text{mCPBA} \text{NaHCO}_3, (79\%)} \text{EtO}_2\text{C} \]

XIV. Provide a complete arrow (electron) pushing mechanism for the following transformations. 
(5 pts)

\[ \text{OH} \text{OSiEt}_3 \xrightarrow{1. \text{PhSeNa, EtOH} (82\%)} \text{OH} \text{OSiEt}_3 \xrightarrow{2. \text{mCPBA, CH}_2\text{Cl}_2 22^\circ\text{C} (95\%)} \text{OH} \text{OSiEt}_3 \]
XV. Addition of the vinyl lithium species to the carbonyl compounds indicated proceeds with complementary stereoselectivity. Noting that the carbonyl compounds differ only in the substitution about the nitrogen, provide explanations for the observed stereochemical outcomes. (8 pts)

![Structures](image1)

XVI. Provide conditions that will stereoselectively convert the β-hydroxy carbonyls shown into their respective syn and anti diols. (8 pts)

![Structures](image2)

XVII. Reaction of E with NaOt-Bu at 0 °C affords compound H. Mechanistic studies suggest that H is formed via aldol addition (E → F), carbonate migration (F → G), and β-elimination. Provide the structures of F and G. (10 pts)

![Structures](image3)

XVIII. Provide a mechanistically based explanation for the observed geometric course of the reaction shown below. (6 pts)

![Structures](image4)
**Bonus Question 1:** During last week’s organic seminar Kunli Liu mentioned the reaction shown below. Provide a complete arrow (electron) pushing mechanism for this multi-component transformation. Hint: The aldehyde and the amine react first followed by the isocyanide, and finally the carboxylic acid. (10 pts)

![Chemical Reaction Diagram]

**Bonus Question 2:** Among my favorite CEM 850 topics was the Felkin-Ahn model. This model is named after Hugh Felkin and Nguyễn Trọng Anh. Felkin’s original model addressed a drawback of the Cram model, namely the invocation of an eclipsed conformation in the transition state between the carbonyl substituent (the hydrogen atom in aldehydes) and the largest $\alpha$-carbonyl substituent. Among Ahn’s improvements was the incorporation of the Bürgi-Dunitz angle. Interesting, Ahn PhD student would go do a post-doc with Dunitz and then begin her independent career at the University of Michigan before taking a position at the University of Paris-Sud and then the Institut Charles Gerhardt Montpellier. Who was she? (2 pts)

(a) Janine Cossy
(b) Odile Eisenstein
(c) Corinne Gosmini
(d) Madeleine Joulie
(e) Marie-Anne Pierrette Paulze