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**BONUS** 8       

Exam Total
1) Draw the detailed arrow pushing mechanism for each step. (12 pts.)
2) Compounds containing a vinyl ether functional group are rather unstable upon exposure to acid, and will decompose to aldehydes. Provide a mechanism that accounts for this instability. (8 pts.)

\[
\begin{align*}
\text{OMe} & \quad \text{HCl} & \quad \text{H}_2\text{O} & \quad \text{H} \\
\text{OMe} & \quad \text{H}_2\text{O} & \quad \text{OMe} & \quad \text{H}^+ \\
\text{OMe} & \quad \text{H}_2\text{O} & \quad \text{H} \\
\text{OMe} & \quad \text{H} \\
\end{align*}
\]

3) Indicate the pKa for the protons shown in the compounds. (2 points if within 2 units, 1 point if within 3 units) (12 pts.)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CN} & \quad \text{H}_3\text{C} & \quad \text{NO}_2 \\
\text{H}_3\text{C} & \quad \text{NO}_2 \\
\text{H} & \quad \text{N} & \quad \text{H} \\
25 & \quad 10 & \quad \sim20 & \quad \sim9 & \quad 8 & \quad 8.8
\end{align*}
\]

4) Write the product that would be expected from the following reaction. Can you think of anything that might go wrong with this reaction? (10 pts.)

Problem with this reaction:
The product from this reaction is also an aldehyde which could react with another molecule of the Wittig reagent.
5) Predict the product and show the mechanism for each step. (14 pts, 4 pts. for the product prediction)

\[
\begin{align*}
\text{Li, NH}_3 & \rightarrow \text{EtI} \\
\text{tBuOH} & \\
\end{align*}
\]

6) The Wittig reactions of unstabilized phosphorus ylides give cis olefins via a phosphaoxetane intermediate. However, the corresponding arsenic ylide gives an epoxide with the same aldehyde. The first step in the reactions of both ylides is a [2+2] cycloaddition. Provide a mechanism to account for the formation of the epoxide from the arsaoxetane. (Show the stereochemistry of the epoxide.) (10 pts., 2 pts. for stereochemistry.)
Consider the hydrolysis of acetals A and B:

\[ \text{A} \quad \text{or} \quad \text{B} \]

a) Which of the two molecules will hydrolyze faster? (2 pts.)

\[ \text{B} \]

b) Draw the oxonium ion intermediate formed from each acetal. (4 pts.)

\[ \text{A'} \quad \text{B'} \]

c) Can you use structures of the oxonium ions to account for which is faster? (2 pts.)

A’ is not stable because of severe ring strain, so the hydrolysis of A will be very slow. B’ does not have such problem.

d) Can you use stereoelectronics to predict which is faster? (Use orbital interactions to illustrate.) (4 pts.)

As shown in the pictures on the right side, for molecule B there is an interaction of the lone pair on the back oxygen and the front C—O σ* bond, which will weaken the C—O bond to facilitate the hydrolysis of the acetal. However, in molecule A there is no such interaction. Thus B will hydrolyze faster than A.
8) Suggest a synthesis of each molecule shown below. (24 pts.)

a. Start from molecules with 8 carbons or less.

b. Synthesize the following molecule from the starting materials provided in the box.

c. Start from pyridine
9) Show a detailed mechanism (including all steps) to account for the following reactions. (16 pts.)

[Diagram showing a mechanism for a chemical reaction]

10) Pyrrole can act as a nucleophile and undergo many different reactions. It has two different carbon sites that can react. Predict the product of the following reaction and explain the regioselectivity. (8 pts.)

[Diagram showing a mechanism for a chemical reaction]

2-position is favored because of more stable carbocation intermediate.
11) LDA is a commonly used non-nucleophilic base to make enolates form carbonyl compounds. However, the first step shown below does not give enolate 2 which is needed for the second step. Suggest a method for making enolate 2 and show a mechanism to account for its formation. (8 pts.)

![Mechanism Diagram](image1)

12) Provide the product of the reaction shown below under both conditions and explain the stereochemistry in each case by showing a mechanism. (14 pts., 4 pts. for product prediction)

![Reaction Diagram](image2)

left side:

![Mechanism Diagram](image3)

right side:

![Mechanism Diagram](image4)
Polyethylene terephthalate (PET) is made by the condensative polymerization of terephthalic acid (PTA) and ethylene glycol. Polybutylene terephthalate (PBT) is made by the condensative polymerization of dimethyl terephthalate (DMT) and 1,4-butaneediol. Attempted reaction of terephthalic acid (PTA) with 1,4-butaneediol will not afford polymeric PBT. (16 pts.)

(a) Identify the structure of the byproduct formed during attempted polymerization of terephthalic acid (PTA) with 1,4-butaneediol that interferes with formation of PBT polymer.

(b) Why does reaction of dimethyl terephthalate (DMT) with 1,4-butaneediol lead to polymer PBT formation?

There is no acid that catalyzes cyclization of the diol to THF in this case.

(c) Why is there no need to use dimethyl terephthalate (DMT) for the synthesis of PET polymer?

Cyclization rules:
Relative reaction rate with respect to ring size: $5 > 6 > 3$

Formation of ethylene oxide (3-membered-ring) from PTA and ethylene glycol is much slower than THF formation from PTA and 1,4-butaneediol.
Indicate the missing products/reactants/reagents for the following reactions. (36 pts).

\[ \text{MeMe}_\text{Ph}O \xrightarrow{\text{NH}_2\text{OH} \cdot \text{HCl}} \xrightarrow{\text{K}_2\text{CO}_3} \text{MeMe}_\text{Br} \xrightarrow{\text{NH}_2\text{OH} \cdot \text{HCl}} \text{NaOEt} \]

\[ \text{O} \xrightarrow{\text{Me}_2\text{CuLi}} \xrightarrow{\text{Me}_3\text{SiCl}} \xrightarrow{\text{MeLi} (1 \text{ eq})} \xrightarrow{\text{PhCH}_2\text{Br}} \]

\[ \text{N} \xrightarrow{\text{POCl}_3} \xrightarrow{\text{EtSH}} \]

\[ \text{SiMe}_3 \xrightarrow{\text{1) n-BuLi}} \xrightarrow{\text{2) EtI}} \xrightarrow{3) \text{NaOH}} \]

\[ \text{AlCl}_3 \]

\[ \text{O} \xrightarrow{\text{AcCl (excess)}} \]

\[ \text{O} \xrightarrow{\text{1) NaH}} \xrightarrow{\text{2) nBuLi}} \]
Who won the Nobel Prize in chemistry for 2012? Robert J. Lefkowitz, Brian K. Kobilka

In which University(ies) was the work done?
Howard Hughes Medical Institute and Duke University Medical Center, Durham, NC, USA & Stanford University School of Medicine, Stanford, CA, USA

Describe the nature of the work for which the award was given.

Studies of G-protein–coupled receptors