Chemistry 334

Examination #1

March 3, 2003

Name: _____________________________

Be certain that your examination has six (6) pages including this one.

Put your name on each page of this examination booklet.

By putting your name on this examination booklet you agree to abide by California State University, Northridge policies of academic honesty and integrity.

Molecular models are allowed for this examination. Calculators are unnecessary and are not allowed.
1. (25 points)

Draw the structure of the expected major organic product for each of the following five (5) questions. Clearly specify stereochemistry, if relevant.

A.

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

\[-78^\circ\text{C}\]

B.

\[
\begin{align*}
\text{OCH}_3 & \quad \text{O} \\
\text{CH}_3 & \\
\end{align*}
\]

\[\text{HNO}_3\]

\[\text{H}_2\text{SO}_4\]

C.

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

\[\Delta\]

D.

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

\[\text{H}_2\text{O}_2\]

E.

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

1.) \text{PBr}_3

2.) \text{PhS}^- \text{K}^+
2. (25 points)

Circle the number that corresponds to the correct answer for each of the following five (5) questions.

A. The allyl radical possesses:
   1. one \( \pi \) electron
   2. two \( \pi \) electrons
   3. three \( \pi \) electrons

B. Alkylamines react with 2,4-dinitrofluorobenzene via:
   1. an electrophilic aromatic substitution mechanism
   2. a nucleophilic aromatic substitution mechanism
   3. a nucleophilic aliphatic substitution mechanism

C. The thermal, cycloaddition reaction of isoprene (2-methyl-1,3-butadiene) with methyl acrylate (\( H_2C=CHCO_2CH_3 \)) affords:
   1. only one enantiomer
   2. a mixture of two enantiomers
   3. a mixture of two diastereomers

D. The \( \Pi_3^* \) molecular orbital of 1,3-butadiene contains:
   1. one node between adjacent carbon atoms
   2. two nodes between adjacent carbon atoms
   3. three nodes between adjacent carbon atoms

E. 1,2-Diels-Alder adducts are formed preferentially over 1,3-adducts due to:
   1. steric hindrance
   2. inductive effects
   3. molecular orbital interactions
3. (15 points)

Draw the mechanism of the following reaction, using the curved-arrow notation to indicate the reorganization of electron density. Show all intermediates and denote all lone pair electrons, formal charges and countercharges where appropriate. Draw all important resonance contributors for intermediates.
In principle, the reaction sequence shown below can give any of the following three products (A, B or C). In reality, only one product is formed. The broadband proton-decoupled $^{13}$C NMR spectrum of the product contains a total of six resonances (excluding resonances due to the solvent and TMS). Use the $^{13}$C NMR data to identify the actual product. Explain concisely why the other isomers can be ruled out, due to the spectroscopic data.
5. (20 points)

Draw the specific reagent(s) necessary to effect the transformation shown, for each of the following two (2) questions. If more than one reaction is involved in an answer, be certain to distinguish the individual steps clearly.

A.

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

(racemic)

B.

\[
\begin{align*}
\text{OCH}_3 & \quad \text{N} & \quad \text{O} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]

(racemic)

Congratulations!

1 /25
2 /25
3 /15
4 /15
5 /20
Total: /100