Spring 2000 Org II E2 Ch 18-19 100 points

NAME:

If you do not wish to have your script placed outside my office, then please check this box.__

1) Name the general class of organic molecules that each of these molecules belong to, and circle the most reactive molecule with respect to undergoing nucleophilic attack. (7pts)

\[
\begin{array}{cccc}
\text{O} & \text{O} & \text{O} \\
R-C-Cl & R-C-H & R-C=\equiv N & R-C-R \\
\end{array}
\]

2) Name the general class of organic molecules that each of these molecules belong to, and draw the Lewis structure including lone pairs for two of the following molecules. (10.5pts)

\[
\begin{array}{ccc}
R-N_2^+ & R-NCO & R-NO_2 \\
\end{array}
\]
3) Circle the stronger base in the following pairs, and in a sentence explain your choice. (10pts)

(a) 

(b) 

(c) 

(d) 

(e) 

H₃C-C-NH₃⁺ CH₃-CH₂-NH₂

H₃C=N-CH₃

H₃C-C-NH

H₃C-C=CN

H₃C-CH₁
4) Name the following compounds in IUPAC acceptable terms. (12 pts)

\[
\begin{align*}
\text{CH}_3\text{CH}2\text{CH}2\text{CH}2\text{CH}=\text{CH}2 & \quad \text{F} & \quad \text{CH}_3\text{CH}2\text{CH}2\text{CH}_2\text{CO}_2\text{H} \\
\end{align*}
\]
5) Explain why in both pairs, the left hand molecule is more reactive toward nucleophilic attack. (10pts)
6) In an attempt to supplement his income, a young chemistry professor decided to synthesize compound B, commonly known as *methamphetamine* by the following route. (2+3+3+3+7=18 pts)

\[
\begin{align*}
\text{(i) what class of organic compound is } A & \text{?} \\
\text{(ii) what reagents are needed to convert the starting material into } A & \text{?} \\
\text{(iii) draw the structure of compound } B. & \\
\text{(iv) what other reagent(s) could accomplish the transformation } A \text{ to } B & \text{?} \\
\text{(v) Draw the mechanism for the transformation of the starting material into } A.
\end{align*}
\]
7) Give the products formed in **five** of the following reactions. (15pts)

(a) \[
\text{CH}_3\text{CN} \quad \text{KCN} \quad \text{A} \quad \text{LiAlH}_4, \text{H}_2\text{O}
\]

(b) \[
\text{Ph} - \text{C} - \text{H} \quad \text{1)} \quad \text{CH}_3\text{MgBr} \\
\quad \text{2)} \quad \text{H}_3\text{O}^+
\]

(c) \[
\text{NH}_2 \\
\text{excess CH}_3\text{CH}_2\text{CH}_2\text{-Br}
\]

(d) \[
\text{H}_3\text{C} - \text{C} - \text{H} \\
\text{1)} \quad \text{Ph}_3\text{P, CH}_3\text{-Br} \\
\quad \text{2)} \quad \text{BuLi} \\
\quad \text{3)} \quad \text{warm}
\]

(e) \[
\text{NH}_2 \\
\text{excess H}_3\text{C} - \text{C} - \text{Cl}
\]

(f) \[
\text{NH}_2 \\
\text{1) excess CH}_3\text{-Br} \\
\quad \text{2)} \quad \text{Ag}_2\text{O, H}_2\text{O, heat}
\]
8) Give reagents for the following reductions, bearing in mind the incompatibility of some of the functional groups. (9pts)

\[ \text{H}_3\text{C}-\text{C}-\text{C}-\text{CH}_2\text{-OH} \]

9) Write the mechanism for the base catalyzed hydration of cyclohexanone (8.5pts)
*Bonus question* (up to 3pts)
The Curtius rearrangement involves the reaction of an acid chloride with a azide anion, to eventually generate an amine. Mechanistically it is identical to the Hoffman rearrangement. Thus, draw the arrows for the key step, which is the rearrangement of the acyl azide into the isocyanate.

\[
\begin{align*}
\text{O} & \quad \text{R-C-N}=\text{N} \\
\rightarrow & \quad \text{R-NCO} \\
& \quad \text{N}=\text{N}
\end{align*}
\]
1) Name the general class of organic molecules that each of these molecules belong to, and circle the most reactive molecule with respect to undergoing nucleophilic attack. (7pts)

2) Name the general class of organic molecules that each of these molecules belong to, and draw the Lewis structure including lone pairs for two of the following molecules. (10.5pts)
3) Circle the stronger base in the following pairs, and in a sentence explain your choice. (10pts)

(a) Pyrrole's lone pair is involved in the aromatic sextet of π-electrons, making it less available for protonation.

(b) Aniline's lone pair is delocalized around the ring, making it less available for protonation.

(c) The oxamide's lone pair is delocalized onto the oxygen, making it less available for protonation.

(d) The cyano group's lone pair is in a higher π-orbital, making it less available for protonation.

(e) The pyridazine lone pair is in a higher π-orbital, making it less available for protonation.
4) Name the following compounds in IUPAC acceptable terms. (12pts)

- Heptan-4-one
- 5-FluoroHexan-2-one
- 2-MethylCyclohexanone
- N-EthylHexan-3-amine
5) Explain why in both pairs, the left hand molecule is more reactive toward nucleophilic attack. (10pts)

\[ \text{Less sterically crowded; easier for nucleophile to attack.} \]

\[ \text{Electronically, the carbonyl carbon is more positively charged (since CF}_3\text{ is electron withdrawing) and therefore the nucleophile is more strongly attracted.} \]
6) In an attempt to supplement his income, a young chemistry professor decided to synthesize compound B, commonly known as methamphetamine by the following route. (2+3+3+3+7=18pts)

(i) what class of organic compound is A?
(ii) what reagents are needed to convert the starting material into A?

(iii) draw the structure of compound B.

(iv) what other reagent(s) could accomplish the transformation A to B?

(v) Draw the mechanism for the transformation of the starting material into A.
7) Give the products formed in five of the following reactions. (15pts)

(a) \[ \text{O} \text{Tos} \rightarrow \text{KCN} \rightarrow \text{A} \rightarrow \text{LiAlH}_4, \text{H}_2\text{O} \rightarrow \text{NH}_2 \]

(b) \[ \text{Ph} - \text{C} - \text{H} \rightarrow 1) \text{CH}_3\text{MgBr} \rightarrow \text{H}_2\text{O}^+ \]

(c) \[ \text{NH}_2 \rightarrow \text{excess CH}_3\text{CH}_2\text{CH}_2\text{-Br} \]

(d) \[ \text{H}_3\text{C} - \text{C} - \text{H} \rightarrow 1) \text{Ph}_3\text{P, CH}_3\text{-Br} \rightarrow 2) \text{BuLi} \rightarrow 3) \text{warm} \]

(e) \[ \text{NH}_2 \rightarrow \text{excess, H}_3\text{C} - \text{C} - \text{Cl} \]

(f) \[ \text{NH}_2 \rightarrow 1) \text{excess CH}_3\text{-Br} \rightarrow 2) \text{Ag}_2\text{O, H}_2\text{O, heat} \]
8) Give reagents for the following reductions, bearing in mind the incompatibility of some of the functional groups. (9pts)

\[
\begin{align*}
\text{H}_3\text{C}-&-\text{C}-\text{C}_{\text{O}} & \text{(or LiAlH}_4) & \text{H}_2\text{O} \\
\text{H}_3\text{C}-&-\text{C}-\text{C}_{\text{O}}& \rightarrow & \text{H}_3\text{C}-&-\text{C}-\text{CH}_2\text{-OH} \\
\text{H}_3\text{C}-&-\text{C}-\text{C}_{\text{O}}& \rightarrow & \text{H}_3\text{C}-&-\text{C}-\text{C}_{\text{O}} \\
\text{H}_3\text{C}-&-\text{C}-\text{C}_{\text{O}}& \rightarrow & \text{H}_3\text{C}-&-\text{CHCH}_{\text{2}}\text{-OH} \\
\end{align*}
\]

9) Write the mechanism for the base catalyzed hydration of cyclohexanone (8.5pts)

\[
\begin{align*}
\text{cyclohexanone} & \rightarrow \text{cyclohexanol} \\
\end{align*}
\]
*Bonus question* (up to 3pts)
The Curtius rearrangement involves the reaction of an acid chloride with a azide anion, to eventually generate an amine. Mechanistically it is identical to the Hoffman rearrangement. Thus, draw the arrows for the key step, which is the rearrangement of the acyl azide into the isocyanate.