Intensive Organic Chemistry for Freshmen Problem Set III

1. What is the expected major product for each of the following reactions?

Due: Feb.16.2001

c) OH
$$\frac{SOCI_2}{N}$$

$$\begin{array}{c|c} \text{d)} & & & \\ \hline & & \\ \hline & & \\ \hline & & \\ \hline \end{array}$$

f)
$$OH$$
 H_2SO_4 \triangle

2. Draw the major product of the following transformation and also show the mechanism in detail (specify stereochemistry)

$$\begin{array}{ccc}
 & OH \\
 & & \\
\hline
 & PBr_3 \\
\hline
 & A \\
\hline
 & S-isomer
\end{array}$$

3. How could you convert starting materials 1 and 2 to products 3 and 4, respectively?

4. What is the major product of the following transformations?

a) OH
$$\frac{(CF_3SO_2)_2O}{N}$$
 A $\frac{NaOH}{THF, H_2O}$ B

$$C)$$
 Br H_2O D

e) +
$$[(CH_3)_2CuCN]Li_2$$
 F

f) HS OTs
$$\frac{\text{NaH}}{\text{DMF}}$$
 G

5. Predict what products will be formed in the following reactions.

DEAD: EtO₂C-N=N-CO₂Et

b) OH
$$\frac{HN_3}{Ph_3P, DEAD}$$
 2

6. Draw structures of all products of the following reactions. Provide an explanation for each case.

a) Br
$$CH_3OH, H_2O$$
 Δ 7

(hint: S_N1 mechanism)

7. Propose a mechanism for the following reaction (Hint: S_N1 mechanism)

8. What is the major product of each reaction? Specify stereochemistry!

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$$\underbrace{\begin{array}{c} 1. \text{ MsCI, Py} \\ 2. \text{ KOH, EtOH} \end{array}}_{\text{OH}} \underbrace{\begin{array}{c} \frac{\text{H}_3 \text{PO}_4}{\triangle} \end{array}}_{\text{OH}}$$
 10

10. The carboxylate ion in the side chains of certain glutamic acid residues of proteins can be sometimes methylated by S-adenosyl methionine to generate an ester. Propose a mechanism for this reaction, showing the expected structure of the product.

11. Explain the following observation.

$$H_3C^{\circ}$$
OH Δ

12. For each pair of reactants, which one do you expect to react faster, why?

a)
$$+ OH^{-} \xrightarrow{H_2O} \rightarrow OH + I^{-}$$

$$+ OH^{-} \xrightarrow{H_2O} \rightarrow OAc + I^{-}$$

b)
$$(CH_3)_3CBr + H_2O \longrightarrow (CH_3)_3COH + HBr$$

 $(CH_3)_2CHBr + H_2O \longrightarrow (CH_3)_2CHBr + HBr$

c)
$$+ HS^{\Theta} \xrightarrow{EtOH} \longrightarrow SH + I^{\Theta}$$

$$CI + HS^{\Theta} \xrightarrow{EtOH} \longrightarrow SH + CI^{\Theta}$$

d)
$$+ Cl^{\Theta}$$
 $+ MsO^{\Theta}$

$$+ PhSe^{\Theta} + MsO^{\Theta}$$
SePh

e)
$$\longrightarrow$$
 Br + N₃ $\stackrel{\bullet}{\longrightarrow}$ \longrightarrow N₃ + Br $\stackrel{\bullet}{\longrightarrow}$ N₄ + Br $\stackrel{\bullet}{\longrightarrow}$ N₄ + Br $\stackrel{\bullet}{\longrightarrow}$ N₅ + Br $\stackrel{\bullet}$