UNIVERSITY OF WINDSOR DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY

Chemistry 59-331/333 Final Examination April 27, 1993 Time: 3 hours

Answer all questions in the exam booklet

1. Do any ten (10)

Indicate the structure of the expected major product from each of the following reactions. Mechanisms are not necessary, but showing your work is likely to be a help. Include product stereochemistry where it applies (**Total 40 marks**).

a)

b)

OH

1) SOCI₂

2) NaN₃, benzene

3)
$$\Delta$$
, MeOII

4) H₃O⁺

c)

d)

MeO₂C
$$CO_2$$
Me 1) NaOMe, MeOH OO_2 C OO_2 Me 2) OOO_2 PH 3

e)

Cl
$$CO_2Et$$
 + CHO 1) KO^tBu, Et_2O 2) $cold NaOlI_{(aq)}$ 3) $NH_4Cl_{(aq)}$

g)

$$OH$$
 MnO_2 , pentane, Δ

h)

OMe
$$+$$
 CO₂Me

i)

$$CO_2Et$$

Br

 CO_2Et
 EtO_2C
 CHO
 CHO
 CHO
 CHO

j)

k)

$$\begin{array}{c} O \\ \text{Ph} \end{array} \begin{array}{c} O \\ \text{DMe} \end{array} \begin{array}{c} \text{BF}_3, \text{CH}_2\text{Cl}_2 \\ \text{OMe} \end{array}$$

l)

2. (Total 20 marks)

a) Draw the <u>complete</u> mechanism for the aldol condensation between two molecules of acetone. Note that the elimination portion is included.

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 O $^{HO^{-}}$, $^{H_{2}O}$, $^{\Delta}$

b) Do i) or ii), but not both

i) The lithium aluminum hydride reduction of amides forms amines, not alcohols. Show by mechanism how this occurs.

$$\begin{array}{c}
O \\
NMe_2
\end{array}$$
1) LiAlH₄, Et₂O
$$\begin{array}{c}
NMe_2
\end{array}$$

ii) Draw the mechanism for the metal acid reduction of α -hydroxy ketones.

3. Do any 8 (eight) of the letter compounds

Give the expected compounds corresponding to the letters below. Include any stereochemistry where it applies. (Total 40 marks)

a)

CO₂Et
$$\xrightarrow{\text{EtO}^-, \text{EtOH}}$$
 A $\xrightarrow{\text{1) NaH, Et}_2\text{O}}$ B

b)
$$\frac{1) \text{BII}_{3}, \text{THF}}{2) \text{II}_{2}\text{O}_{2}, \text{NaOII}} \quad C \quad \frac{\text{II}_{2}\text{O}_{3}, \text{H}_{2}\text{SO}_{4},}{\text{II}_{2}\text{O}_{3}, \text{acetone}}}{2) \quad \text{CI}_{2}\text{CO}_{3}\text{II}} \quad D$$

d)

e)

$$CH_{3}O-CH_{2}Cl \xrightarrow{2) \text{ BuLi, Et}_{2}O} I \xrightarrow{1.05 \text{ equiv LDA,}} J$$

$$CH_{3}O-CH_{2}Cl \xrightarrow{3)} CHO \qquad I \xrightarrow{-78^{\circ}, \text{ THF}}$$

$$2) \text{ add } I$$

$$4) \text{ II}_{3}O^{+}_{(aq)} \qquad 3) \text{ NII}_{4}Cl_{(aq)}$$

4. Show by equation how you could prepare the products illustrated below from the given starting material. You may use any other reagents you deem fit. Show all reagents, conditions, and isolable intermediates. Mechanisms are not necessary, but may be a help. (Total 70 marks) Do any seven (7)

a)

b)

c)

d)

e)

$$Ph = N$$

$$Ph$$

$$Ph$$

$$SPh$$

f)

g)

h)

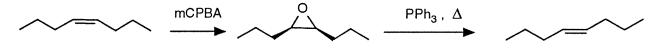
i)

$$\stackrel{O}{\longleftarrow}$$

Bonus (up to 10 marks):

a) The Wadsworth-Horner-Emmons reagent, which is so widely used in Wittig type reactions, is prepared by the Arbuzov reaction, which is simply a thermal reaction between an alkyl halide and a trialkyl phosphite. Can you suggest a reasonable mechanism for this reaction?

b) One of the methods for inverting the stereochemistry of a double bond involves creating an epoxide, and then treating the epoxide with triphenyl phosphine (see below). How does the second half (from the epoxide on) of the process occur?



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