UNIVERSITY OF WINDSOR SCHOOL OF PHYSICAL SCIECNES CHEMISTRY AND BIOCHEMISTRY

Chemistry 59-634 Final Examination

Dec. 20, 1999 Due. Dec. 21, 1999

- 1. **(50 marks)** Provide the major reaction product in each of the following transformations. Include stereochemical (relative and or absolute) information where it is relevant. <u>Please show your work</u>, i.e., intermediates and rationalizing the reasons for something occurring in the indicated manner.
- a) Note: Allenylsilanes react in a manner directly analogous to allylsilanes.

MeO
$$BF_3$$
-OEt₂, CH₂Cl₂ $A \longrightarrow SiMe_3$
 $H_2C=C \longrightarrow SiMe_3$
 $CpCo(CO)_2$, hv toluene, Δ

b) $Pd(OAc)_{2}, \qquad C$ $PPh_{3(cat)}, NEt_{3}, \Delta$ $Ag_{2}CO_{3}$ What would you get if you used this compound instead? D

d) $AcO \longrightarrow CH_3 \qquad \underbrace{\frac{1) \text{ Fe}_2(CO)_9, \text{ Et}_2O, \Delta}{2) \text{ OSiMe}_3, \text{ CH}_2CI_2, -78}^{OSiMe}_3}_{OEt \text{ BF}_3} \text{ F}$

e) Presuming you could really make the following starting material, and assuming that those alkyls are electron *donating*.

f)

Br
$$\xrightarrow{1) \text{CpFe}^-(\text{CO})_2 \text{Na}^+}$$
 H $\xrightarrow{1) \text{n}_{\text{Bu}_2\text{CuLi}, Et}_2\text{O}}$ 1

2)AgSbF₆ + O CI 2) (NH₄)₂Ce(NO₃)₆, MeOH

g) There are certain elements of the *relative* stereochemistry in the product which are beyond the scope of this course.

2. Show by equation how you would prepare the illustrated below from the given starting material. You may use any other reagents that you deem fit, but the intent is to focus on material learned in this course. Show all reagents, conditions, and intermediates. Mechanisms are not necessary, but may be a help. (Total 50 marks)
a)

e)
$$\begin{array}{c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & \\ & & \\ & \\ & & \\ & \\ & & \\ & & \\ & \\ & \\ & & \\ & \\ & & \\ & \\ & & \\ & \\ & \\ & \\ & \\$$

3. (10 marks) The following two closely related reactions go in very different directions. The enyne on the left follows the 'expected' pathway, whereas the diene on the right gives the surprising, initially unexpected product. Give the 'expected' product for the left transformation and discuss how the 'unexpected' product on the right come about, in detail.

$$\begin{array}{c|c}
 & & & \\
 & & \\
\hline
 &$$