Chemistry 234 Organometallics Problem Set

1) For each compound below, draw an arrow to indicate the direction of the bond dipole in each. Label each species as an electrophile (electrophilic C) or nucleophile (nucleophilic C).





2) Show the products of reaction between each organometallic reagent below with the given proton source.

a. $+ H^{O_{H}}$

c. \longrightarrow Li + $_{D}$, \bigcirc \bigcirc

e. MgBr + HS ---

3) Show how 1-bromopropane is converted to an organolithium species, an organomagnesium species, and an organocuprate.

- 4) Predict the product of the reaction between each organohalide and Gilman reagent shown below.
 - a. Et₂CuLi +
 - **b.** $(CH_3)_2CuLi$ + \nearrow Br
 - **c.** (CH₃)₂CuLi +
 - d. ()2CuLi + Cl
 - e. Bu₂CuLi +
 - f. Et_2CuLi + Cl
- 5) Predict the product for the reaction involving each organomagnesium or organolithium compound shown below. Assume an excess of organometallic reagent.
 - a. 1. PhMgBr 2. Dilute H+
 - b. $\frac{0}{H}$ $\frac{1. Li}{2. \text{ Dilute H}^+}$
 - c. H₃CO 1. PhMgBr 2. Dilute H+
 - d. O $1. CH_3Li$ $2. Dilute H^+$
 - e. 0 1. MgBr 2. Dilute H+
 - f. CO_2 1. EtMgBr 2. Dilute H⁺

6) Show the complete electron pushing mechanism for the reaction in 5c.

7) Show the complete electron pushing mechanism for the reaction shown in 5f.

8) When performing a Grignard reaction, a dimerization byproduct is frequently encountered. Propose a mechanism that leads to this dimerization product.

$$\bigcirc$$
Br $\stackrel{\mathsf{Mg}}{\longrightarrow}$

9) A chemist tried to carry out the following reaction in the lab. The desired product was not isolated. Explain what went wrong.

- 10) Show the oxidative addition of bromobenzene to palladium metal.
- 11) Show the reductive elimination of the intermediate below to form a new carbon-carbon bond.

12) Predict the product for each Suzuki reaction shown below.

a.
$$+$$
 B_0 OH^-

c.
$$Ph-B$$
 OR $Pd(PPh_3)_4$ OH-

d.
$$Ph$$
 OR Ph OR $Pd(PPh_3)_4$ OH

13) What starting materials would be required to prepare the product shown below via a Suzuki coupling reaction?

14) Show how you could prepare the following organoborane starting with catechol borane, benzene, and any other organic or inorganic reagents. Hint: It will take 3 steps to convert benzene to the species that reacts with catechol borane.

15)Predict the product(s) for each Heck coupling reaction shown below.

a.
$$H_2C=CH_2$$
 $Pd(OAc)_2$ PPh_3, NEt_3

b.
$$Pd(OAc)_2$$
 PPh₃, NEt₃

c.
$$Pd(OAc)_2$$

$$PPh_{3}, NEt_3$$

16) What organohalide can be coupled with styrene to produce each of the compounds shown below via a Heck coupling reaction?