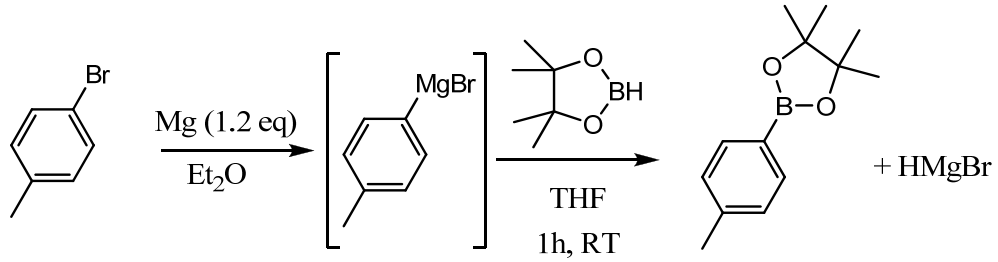
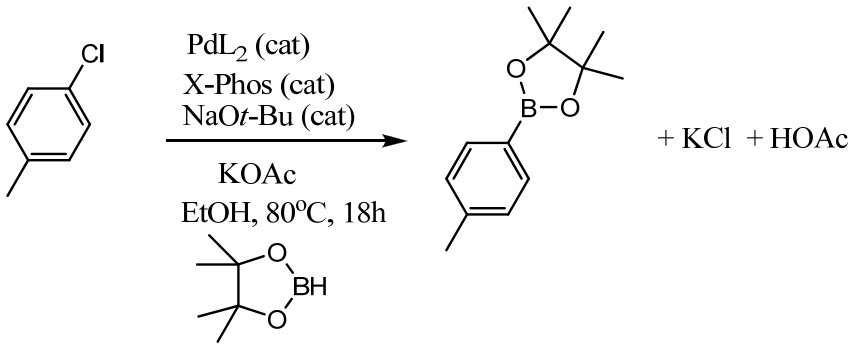
Chem 253—Green Chemistry in-class problems

One way to build complex molecules, such as pharmaceuticals and pesticides, is by utilizing a Suzuki coupling reaction. This versatile and Nobel Award-winning coupling reaction requires precursors with a carbon-boron bond, usually borate esters. They can often be problematic to synthesize. Below you will find two different approaches to the synthesis of borate esters.

Classic Borate Ester Synthesis



Modified Borate Ester Synthesis



Note: the combination of Pd, X-Phos and sodium tert-butoxide create the catalyst for the modified reaction. They are used at a level of 1 mol % in the system, and are recycled from one reaction to the next.

1) (10 pts) Calculate the atom economy for each reaction. You can ignore catalysts, since their amounts are small and they are generally reused. How do you deal with solvents in these calculations?

$$C_7H_7Br + 1.2\ Mg + C_6H_{13}O_2B \longrightarrow C_{13}H_{19}BO_2$$

MW: 171.46 29.16 128.00 218.13

$$\%AE = \frac{218.13}{171.16 + 1.2(29.16) + 128} \times 100\% = 66.36\%$$

$$C_7H_7Cl + KO_2C_2H_3 + C_6H_{13}O_2B \longrightarrow C_{13}H_{19}BO_2$$

MW: 126.59 98.15 128.00 218.13

$$\%AE = \frac{218.13}{126.59 + 98.15 + 128} \times 100\% = 61.83\%$$

Solvents are generally not included in the atom economy calculation

2) (6 pts) Using the 12 principles of Green Chemistry and the information from last week's lecture, give three of the principles which have been used in the modified synthesis, and explain the specifics of how these alterations make the modified reaction "greener" than the classic synthesis.

#9—catalytic is better than stoichiometric: Using catalytic metals makes for less toxic reagents used in the synthesis

#10—inoccuous byproducts: Magnesium salts vs. Acetic acid (which can actually be captured and sold off to improve atom utilization in the reaction)

#12—minimize risks: Ethereal solvents vs ethanol—flammability, flashpoints, volatility Grignard reagents—EXTREMELY water reactive and pose explosion hazards

(it is clear that atom economy is NOT favoring the new reaction as the equations are written)

3) (4 pts) You have created a new pesticide. Based on what you know about green chemistry, what general factors do you have to consider about the manufacturing process in order to assess how to make the greenest possible reaction?

Assess the hazards associated with the reagents (toxicity of starting materials, solvents, products, etc), reaction conditions/safety of reaction, efficiency of the reaction (atom economy), and what happens after the reaction (byproducts, environmental polution, biomagnification, etc)