University of Windsor Department of Chemistry and Biochemistry 59-531 Midterm Exam

Time: 55 minutes Mar. 8, 2007

1. Provide a reasonable mechanism for the two step amination process (we'll call the addn of H₂O in step 3 trivial) for lithiated arenes. Include all mechanisitic steps, and provide at least one reasonable valence bond structure for each intermediate/product (10 marks).

2. Indicate the structure of the major expected product of each of the following transformations. Include the product stereochemistry where it applies. Give the reasoning behind your answer (i.e., show your work) to the degree that's possible in a 1h exam. I also wish to see any intermediates that could be isolated along the way (35 marks).

a)

There's something wrong somewhere in this series of reactions. What is it?

1)
$$H_2SO_{4,}$$

$$\frac{\text{wet } CH_3COOH}{2) \text{ HO}^{-}_{(aq)}, \Delta} \quad D \xrightarrow{\text{iPr}_2NEt, THF} E \xrightarrow{\text{TiCl}_3, H_2O} F$$

$$THPO \qquad NO_2$$

3. Show by equation how you would prepare the products illustrated from the given starting material. You may use any other reagent you deem fit. Show all reagents, conditions, and intermediates that could be isolated. Mechanisms are not necessary, but showing your work may be a help (30 marks).

Bonus: In an attempt to make a sodium enolate of a ketone, a graduate student used an α -bromo ketone and sodium metal. Unfortunately, the student was not aware of how rigourously THF must be dried, and used it right out of the bottle. The reaction's product mixture contained a substantial amount of carboxylic acid. What happened?