**110b Exam 3 Review Sheet- Spring Semester 2020**

**Review Session: Wednesday, March 11, 7:00 PM, SN Aud**

**Examination: Friday, March 13, 7:50 & 8:50 AM, SN Aud**

**Chapter 18:**

1. Acidity of the -hydrogen of carbonyl compounds; know the pKa’s of acetone, nitromethane, and acetonitrile. Why are these hydrogens acidic? What does an enolate ion look like? 10E: 832-833, 11E: 822-823.

2. Keto-enol tautomerism; rationalize the preferred keto form on the basis of select bond strengths. 10E: 833-834, 11E: 823-825.

3. Why do certain optically active aldehydes and ketones racemize easily? 10E: 834-836, 11E: 825-827.

4. Know the mechanisms of base-promoted  -halogenation of aldehydes and ketones and the haloform reaction. Be familiar with the HVZ reaction in terms of reactants, reagents, and product. What is the synthetic utility of these reactions? 10E: 837-841, 11E: 827-831.

5. Lithium enolates. Thermodynamic and kinetic enolates. Using pKa values to predict equilibria in enolate formation. Quantitative vs. non-quantitative deprotonations. Alkylation of lithium enolates. 10E: 841-843, 11E: 831-834.

6. Direct alkylation of esters and nitriles using lithium diisopropylamide (LDA). 10E: 843, 11E: 833.

7. -dicarbonyl compounds, pKa of proton located between the two carbonyl groups. Why is this proton so acidic? 10E: 844-845, 11E: 834-835.

8. The acetoacetic ester synthesis of substituted acetones. Know the step-by-step mechanism of reaction. Break it up into the four steps: 1. Deprotonation, 2a. Alkylation #1 (know limitations), 2b. Alkylation #2 (can be same or different from #1), 3. Saponification (hydrolysis) of the ester under basic conditions, 4. Acidification with heating to decarboxylate (lose CO2). Be aware that the acetoacetic ester anions can also be acylated, and that their dianions can be alkylated. 10E: 845-849, 11E: 835-839.

9. The malonic ester synthesis of substituted acetic acids. Know the step-by-step mechanism of reaction. Break it up into the four steps: 1. Deprotonation, 2a. Alkylation #1 (know limitations), 2b. Alkylation #2 (can be same or different from #1), 3. Saponification (hydrolysis) of the esters under basic conditions, 4. Acidification with heating to decarboxylate (lose CO2). 10E: 850-854, 11E: 840-843.

10. The Stork enamine reaction. Mechanism of formation, mechanism of enamine reaction with electrophiles. 10E: 854-856, 11E: 844-847.