Chem 302, S12
Exam 3 Review Sheet

Chapter 18: acidity of α-hydrogens due to electron-withdrawing inductive and resonance effect of carbonyl; NO_2 group and CN group can also have enhanced acidity of α-hydrogens; keto-enol equilibrium; two reactions that require α-hydrogens (acid or base catalyzed): common intermediate is the enolate anion in base and is the enol in acid, (1) racemization, (2) halogenation; alkylation at the α-carbon: direct method using HO^- or RO^- is not useful (why?); (solution #1) direct method using lithium enolates; (#2) indirect method using β-dicarbonyls as synthetic intermediates, hydrolysis and decarboxylation, including mechanism for decarboxylation, acetoacetic ester synthesis for substituted methyl ketones; malonic ester synthesis for substituted carboxylic acids; (#3) enamines as enolate surrogates

Chapter 19: 4-step mechanism for Claisen condensation of esters to form β-keto esters, why is step 4 necessary?, requires a full equivalent of base and two α-Hs, what is the true product?; Dieckmann condensation (intramolecular Claisen), crossed Claisen; aldol reaction, dehydration of β-hydroxy carbonyl compound gives an α,β-unsaturated compound; intramolecular aldol reactions (formation of 5- and 6-membered rings is favored); crossed aldol reactions, ways to circumvent potential problems; reactions of α,β-unsaturated carbonyl compounds: simple versus conjugate addition, Michael addition (nucleophile is an enolate)

Chapter 20: amine basicity, inductive and resonance effects, use/interpret/analyze pKb values; predict which molecule is a stronger base; preparation of amines: (1) 1^o alkyl amines formed by alkylation of ammonia (overalkylation is a problem) (2) Gabriel synthesis (3) reduction of amides and nitriles with $LiAlH_4$; (4) reductive amination; (5) aromatic nitration followed by reduction; which of the above reactions form only 1^o amines, which reactions can form 1^o, 2^o, 3^o amines; make sure you get some sleep before the exam; reactions of amines: (1) reactions of amines with nitrous acid; how to generate nitrous acid; (2) reactions of aryl diazonium salts to form aryl halides, aryl nitriles, phenols, reduction of aryl diazonium group to H; use of aryl diazonium salts in the context of aromatic synthesis; diazo coupling, (3) Hofmann elimination of quaternary ammonium hydroxide to give the less substituted alkene

Chapter 21: phenol acidity, inductive and resonance effects, use/interpret/analyze pKa values; predict which molecule is a stronger acid; best preparation of phenols is starting with $Ar\text{-}N_2^+$; reactions of phenols: (1) ArO- as a nucleophile; (2) HO is a strongly activating o,p-directing group; appropriate conditions can control the outcome of nitration, bromination; aryl halides are unreactive under typical SN1 or SN2 conditions; under certain conditions, Ar-X will undergo substitution via two types of nucleophilic aromatic substitution: the addition-elimination mechanism (o,p withdrawing groups speed the reaction); the elimination-addition mechanism; structure of benzyne

We did not cover the following sections:
18.3D
19.4D, 19.8
20.3F, 20.4E, 20.5A, 20.9, 20.10, 20.11
21.4B, 21.7, 21.9, 21.10, 21.11C, 21.12